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ii, 443	3*	" "HORSR" " "HORSCH."
ii, 529	15*	" "chlchloroform" " "iodoform."

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1386 6* for "latter" read "heat of formation of methane."

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ii, 563 col. ii. insert "Jackson, Leonard C., mathematical investigation of the stability of A. W. Stewart's atom, ii, 405."

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56 Table V. in third column for $\begin{Bmatrix} 5.74 \\ 6.62 \\ 5.15 \end{Bmatrix}$ read $\begin{Bmatrix} 57.4 \\ 66.2 \\ 51.5 \end{Bmatrix}$

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Page, Line.
i. 75 13 }
14 } for "Chelidoneum" read "Chelidonium."
i 131 18* }
5* } ,, "Heterotropic" ,, "Heterotrophie."

* From bottom.

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JOURNAL
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TRANSACTIONS.

I.—A New Modification of 3:4-Dinitro-
dimethylaniline.

By HERBERT SWANN.

DURING an investigation of the nitration of *m*-nitrodimethylaniline, it was found that by varying the conditions of nitration, a new modification of 3:4-dinitrodimethylaniline was formed. This brings 3:4-dinitrodimethylaniline into line with other nitroanilines, most of which exist in at least two modifications (Hantzsch, *Ber.*, 1910, **43**, 1654).

Romburgh (*Rec. trav. chim.*, 1887, **6**, 250) states that *m*-nitrodimethylaniline is readily nitrated by nitric acid (D 1·2), giving the 3:6- (m. p. 112°) and the 3:4- (m. p. 176°) dinitro-compounds. However, by nitrating *m*-nitrodimethylaniline in certain concentrations of sulphuric acid, and using the requisite quantity of nitric acid to introduce one nitro-group, there results a β -modification of 3:4-dinitrodimethylaniline in addition to the 3:6-dinitro-derivative obtained by Romburgh.

β -3:4-Dinitrodimethylaniline is an orange-coloured compound melting at 154°. It is possible to convert it into the α -compound (m. p. 176°) by dissolving in concentrated sulphuric acid and diluting the resulting solution with water, when the α -modification separates, melting at 176° after one recrystallisation from alcohol. The β -compound was also readily changed to the α -compound by boiling an amyl-alcoholic solution with a few drops of 80 per cent.

sulphuric acid. On cooling, the α -modification separated in long needles. No method of changing the α - to the β -compound has yet been found.

Nitration of the β -modification with 70 per cent. nitric acid at 30° gives principally 2:4:5-trinitrodimethylaniline (m. p. 196°), which is also obtained by the nitration of 2:5- and α -3:4-dinitrodimethylaniline under the same conditions. The quantity nitrated was too small for the identification of any other trinitro-compound.

The action of more concentrated nitric acid on the above three dinitrodimethylanilines is of interest. Treatment with nitric acid of about 80 per cent. strength results in a simultaneous nitration and oxidation, a trinitromonomethylaniline being formed. A similar oxidation occurs on nitrating dimethylaniline in acetic acid solution, when under certain conditions 2:4-dinitromonomethylaniline is obtained in good yield.

The trinitromonomethylaniline is a yellow, crystalline compound melting at 199° . Its constitution was proved by replacing the mobile *m*-nitro-group by the methoxy-group, when 4:6-dinitromethyl-*m*-anisidine (m. p. 198°) was obtained. The original compound is therefore 2:4:5-trinitromonomethylaniline.

EXPERIMENTAL.

Preparation of m-Nitrodimethylaniline.

The *m*-nitrodimethylaniline was obtained by the cold nitration of dimethylaniline, as suggested by Nöling and Fourneau (*Ber.*, 1897, **30**, 2931). It was found possible to use much less sulphuric acid in the nitration, thereby facilitating the final neutralisation.

Dimethylaniline (250 c.c.) was dissolved in sulphuric acid (475 c.c.), and the solution cooled in a freezing mixture of ice and salt. The cooled nitrating acid, consisting of 100 c.c. of nitric acid (D 1.5) and 475 c.c. of sulphuric acid, was then added gradually, the temperature being maintained between 0° and 4° . When the whole of the acid had been added, the liquor was poured on ice, and finally diluted with about 20 litres of water, which precipitated the *p*-nitrodimethylaniline. The *m*-nitrodimethylaniline contained in the filtrate was separated by neutralisation with sodium carbonate and crystallised from alcohol, the yield of pure material (m. p. 66°) being about 50 per cent. of the theoretical.

β -3:4-Dinitrodimethylaniline.

Fifty grams of *m*-nitrodimethylaniline were dissolved in 500 c.c. of 60 per cent. sulphuric acid, and to this solution (at 20°) 50 c.c.

of 30 per cent. nitric acid were added, the whole being well shaken. After a few minutes the temperature rose to 35° , and the 3:4-dinitrodimethylaniline separated as an orange-coloured, flocculent precipitate. The liquor was diluted with 250 c.c. of water and filtered, when practically the whole of the β -3:4-dinitrodimethylaniline was obtained in the precipitate, the 2:5-isomeride remaining dissolved in the filtrate. The β -3:4-dinitro-compound after one crystallisation from alcohol or benzene melted sharply at 154° , the yield being 60 per cent. of the theoretical.

Found: N=19.7.

$C_8H_8O_4N_2$ requires N=19.9 per cent.

By considerable dilution of the filtrate, the 2:5-isomeride separated; after crystallisation from glacial acetic acid it melted at 112° .

α -3:4-Dinitrodimethylaniline.

This compound was obtained by nitrating *m*-nitrodimethylaniline (1 gram) with 20 per cent. nitric acid (10 c.c.).

It was also prepared by dissolving the β -modification (5 grams) in sulphuric acid (30 c.c.) and gradually diluting the solution with cold water, the temperature not being allowed to rise above 40° . By this method, the β -compound was completely converted into the α -modification, which, after crystallisation from alcohol or acetone, melted at 176° .

Preparation of 2:4:5-Trinitromonomethylaniline.

Twenty grams of 2:5-dinitrodimethylaniline (or α - or β -3:4-dinitrodimethylaniline) were dissolved in 80 c.c. of nitric acid (D 1.40). The temperature was raised to 30° , and 40 c.c. of nitric acid (D 1.50) were quickly added. After a few minutes, a vigorous oxidation took place, as shown by the evolution of nitrous fumes. At this point the solution was cooled rapidly, and, when the oxidation was finished, poured on ice. The precipitate was collected and digested with 500 c.c. of boiling water for several hours to hydrolyse any tetranitrophenylmethylnitroamine which might have been formed. The *m*-nitro-group in 2:4:5-trinitromonomethylaniline is not removed by boiling water. After hydrolysis, the liquid was filtered hot, and the residual solid crystallised from acetone. A moderately good yield of 2:4:5-trinitromonomethylaniline, a bright yellow, crystalline compound melting at 199° , was obtained.

Found: N=22.8.

$C_7H_5O_6N_3$ requires N=23.1 per cent.

Nitration of 2:4:5-trinitromonomethylaniline with nitric acid (D 1.50) gives 2:4:5:6-tetranitrophenylmethylnitroamine. Treatment of the boiling methyl-alcoholic solution (2 grams in 100 c.c. of methyl alcohol) with the theoretical quantity of potassium hydroxide (0.5 gram) dissolved in the minimum amount of water furnishes 4:6-dinitromethyl-*m*-anisidine (m. p. 198°), thereby establishing the constitution of the original compound as 2:4:5-trinitromonomethylaniline.

The possibility of the above trinitromonomethylaniline containing a nitro-group as a nitroamine was tested by heating with phenol and sulphuric acid in boiling amyl alcohol, but with negative result.

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II.—The Chloroacetates of *S*-Alkylthiocarbamides.

By JOHN TAYLOR.

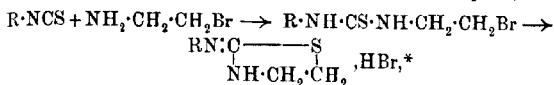
IN a previous communication (T., 1917, **111**, 650), the theory was advanced that salts of *S*-alkylthiocarbamides have a sulphonium structure, $(\text{NH}_2)_2\text{C}:\text{SRX}$, where R is an alkyl group and X an acidic residue. The possibility of the existence of ammonium and of carbonium forms, $\text{XNH}_3\text{C}(\text{NH})\cdot\text{SR}$ and $(\text{NH}_2)_2\text{CX}\cdot\text{SR}$, was considered.

The behaviour of the nitrites and thiocyanates of these compounds points to the improbability of an ammonium structure, whilst the ready ionisation of the salts points to the non-existence of carbonium structure. Occasionally, in the presence of strong acids, a second form of a salt is obtained differing considerably from that separating from a neutral solution. This second form is unstable, being readily converted into the first by recrystallisation from hot water. It was conjectured that this unstable form is of the ammonium type, its instability being paralleled by the instability of the salts of amides.

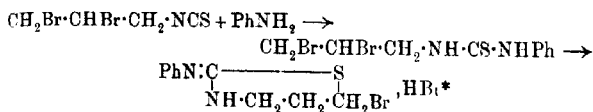
A study of the chloroacetates of *S*-alkylthiocarbamides, and in particular of the monochloroacetates, confirms the view that the salts have not an ammonium structure.

They are readily prepared by mixing a concentrated aqueous solution of thiocarbamide methyl nitrate or of thiocarbamide benzyl chloride with a solution of the sodium salt of the required acid, when the new compound separates from solution.

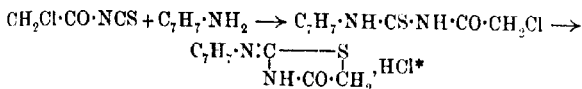
To the general rule that a thiocarbamide results from the interaction of a thiocarbimide and a primary or a secondary amine, there is one tolerably well-marked exception, namely, when the radicle of either contains a halogen constituent. In this case, although the primary union may run the normal course, there follows the production of a salt of a cyclic base in which the carbon atom, originally halogenated, is now attached to sulphur, thus:



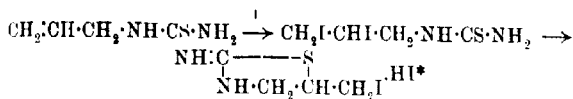
(Gabriel, *Ber.*, 1889, **22**, 1148). Similarly,



(Dixon, T., 1897, **71**, 617). A similar behaviour is shown by halogen-substituted acylthiocarbimides:



(Dixon, *loc. cit.*). The same change results when an already formed non-halogenated thiocarbamide has halogen introduced into its molecule:



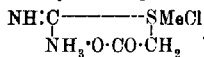
(Dixon, T., 1896, **69**, 25).

Only two exceptions to this rule appear to exist, namely, (1) where halogen is attached to an aromatic radicle, thus the compound $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ is quite stable (Losanitsch, *Ber.*, 1872, **5**, 156), and (2) where halogen is part of an unsaturated radicle; thus the compound $\text{CH}_2\cdot\text{CCl}\cdot\text{CH}::\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ does not yield a cyclic compound (Henry, *Ber.*, 1872, **5**, 188; Dixon, T., 1901, **79**, 553).

It is clear, from these examples, that there is, in thiocarbamides, a very strong tendency towards the conversion of bivalent into quadrivalent sulphur when there is present a halogenated radicle not already linked to sulphur.

* These formulæ are written as the authors themselves gave them. The present author prefers to represent them as sulphonium compounds.

If thiocarbamide methyl monochloroacetate had an ammonium structure, that is, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\cdot\text{NH}_3^+\text{C}(\text{NH})\cdot\text{SMe}$, there would follow the formation of a cyclic compound,



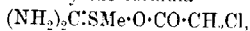
Such a union occurs as the initial stage of the formation of thetines.

This compound would have its chlorine highly ionised, it would respond to Andreasch's test for thioacetic acid (*Ber.*, 1879, 12, 1385), and, further, the chloroacetate group, being now divided into two parts, could not be displaced wholly by another acid group.

Thiocarbamide methyl chloroacetate, prepared as described, agrees in no respect with these properties. Its aqueous solution does not yield silver chloride on the addition of silver nitrate, no purple colour is observed on applying Andreasch's test, hence the compound does not contain the grouping $\cdot\text{CO}\cdot\text{CH}_2\cdot\text{S}\cdot$, and, lastly, the picrate is identical with that obtained from thiocarbamide methyl nitrate, consequently the whole of the chloroacetate group has been displaced by the picrate residue.

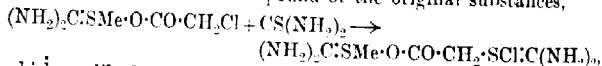
It is thus highly probable that the chloroacetate group is not attached to nitrogen, and that, since ring closing does not occur, the chlorine forms part of a group already linked to sulphur which is already exerting its full valency, and therefore does not admit of further combination.

The structure of thiocarbamide methyl chloroacetate would appear to be represented by the formula

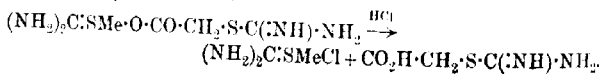


in agreement with that proposed for other salts of *S*-alkylthiocarbamides, and would correspond with its properties as described above.

That the chlorine of the chloroacetate residue would combine with sulphur if opportunity occurred is shown by the fact that, when this substance is heated in alcoholic solution with thiocarbamide, *isothiohydantoic* acid results. This is due to the initial formation of an additive compound of the original substances,



which readily loses hydrogen chloride. The acid, in turn, decomposes the methyl- ψ -thiourea ester of *isothiohydantoic* acid, leaving free *isothiohydantoic* acid.



When thiocarbamide benzyl chloroacetate instead of the methyl compound is combined with thiocarbamide, loss of hydrogen chloride alone follows, and the benzyl- ψ -thiourea ester of isothiohydantoic acid is obtained, showing that the reaction proceeds in the manner suggested.

Attempts to remove hydrogen chloride alone from thiocarbamide methyl chloroacetate by the use of dilute alkali or of pyridine were quite unsuccessful. No indication of the formation of a glycine derivative was observed; the whole of the chloroacetate group was removed and the resulting ψ -thiourea decomposed.

Thiocarbamide and methyl chloroacetate unite additively on long contact in acetone solution. The product is isomeric with the thiocarbamide methyl chloroacetate previously described. There are many points of difference between the two substances; thus the additive compound is readily soluble in water, and the solution is acid, due to the formation of hydrochloric acid. When boiled in alcoholic solution, it loses methyl alcohol, and the hydrochloride of isothiohydantoic acid separates on cooling. With less than one equivalent of sodium hydroxide, both methyl alcohol and hydrochloric acid are lost and isothiohydantoin is obtained. The substance also readily responds to tests for thiolacetic acid.

These reactions are in sharp contrast with those previously described for thiocarbamide methyl chloroacetate, and point to the additive compound being the *hydrochloride of methyl isothiohydantoate*, $(\text{NH}_2)_2\text{C}:\text{SCl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$. Ethyl chloroacetate combines similarly with thiocarbamide.

Dichloroacetates and trichloroacetates of S-alkylthiocarbamides were also prepared. In general properties they closely resemble the monochloroacetates, with the exception that they are inert towards thiocarbamide.

EXPERIMENTAL.

Thiocarbamide methyl monochloroacetate is precipitated when to a concentrated aqueous solution of thiocarbamide methyl nitrate is added an excess of a concentrated aqueous solution of sodium monochloroacetate. On crystallisation from alcohol, it forms prisms, which decompose at about 157° . Its aqueous solution is neutral and furnishes a picrate, melting at 220° , identical with the picrates from other salts of S-methylthiocarbamide. The monochloroacetate responds to the usual tests for S-methylthiocarbamides; an alkaline solution of lead acetate gives lead mercaptide, and an ammoniacal solution of silver nitrate gives silver mercaptide and silver cyanamide, no silver chloride being formed.

Found: $N=15.01$, and 100 parts gave 168 parts of silver as $AgSMe$ and Ag_2CN_2 .
 $C_4H_9O_2N_2ClS$ requires $N=15.17$ per cent., and 100 parts require 175 parts of silver.

When the solid was heated with one equivalent of pyridine, methyl mercaptan escaped. Addition of one equivalent of *N*-sodium hydroxide to a dilute solution of the substance did not cause a precipitation of methyl- ψ -thiourea. When the alkaline solution was acidified with chloroacetic acid and then evaporated, the original substance was recovered. Attempts were made at various stages to obtain a copper derivative of glycine, but quite unsuccessfully.

Thiocarbamide benzyl monochloroacetate was prepared similarly from thiocarbamide benzyl chloride and sodium monochloroacetate. Water and alcohol each dissolve the substance readily, but it is sparingly soluble in a solution of sodium monochloroacetate. The usual reactions of a ψ -thiourea are given, and it yields a *picrate* which melts at 183° .

Decomposition occurs on heating to 156° .

Found: $Cl=13.4$; $N=10.65$.

$C_9H_{11}O_2N_2ClS$ requires $Cl=13.63$; $N=10.74$ per cent.

Attempts to prepare sulphonium and ammonium forms of this compound were unsuccessful. Benzyl- ψ -thiourea dissolved in chloroacetic acid gave an uncrystallisable syrup. The ammonium form of thiocarbamide benzyl sulphate, on treatment with an acid solution of sodium monochloroacetate, yielded the same product as the sulphonium form gave when treated with a slightly alkaline solution of the same salt. Both were identical with the compound already described, and decomposed at the same temperature, namely, 157° .

Thiocarbamide methyl monochloroacetate and Thiocarbamide.
 —Alcoholic solutions of these substances in nearly equivalent proportions (the thiocarbamide in slight excess) were heated together on a steam-bath. After a short time, the liquid, originally clear, became turbid, and a white, amorphous solid separated which contained chlorine, and when heated with an alkaline solution of lead acetate gave, first, lead mercaptide, and, on prolonged heating, lead sulphide. It responded also to Andreaseh's test for thiolacetic acid, thus showing the formation of a derivative of isothiohydantoic acid. The mother liquors gave a strong reaction for ψ -thiourea. Analysis of the first product gave no decisive figures and indicated a mixture. After the solid had been further heated with a further quantity of alcohol, the ψ -thiourea reactions became very faint.

The analysis and general properties of the solid now showed it to be rather impure *isothiohydantoic acid*. The substance chars at about 205° (Found: N=20.1; S=23.1. $C_3H_5O_2N_2S$ requires N=20.9; S=23.88 per cent.).

Thiocarbamide benzyl monochloroacetate and Thiocarbamide.—Combination was effected as in the preceding case. The product, free from chlorine, gave a strong reaction for ψ -thiourea, and responded to the tests for thiolacetic acid. It decomposed on heating to 190°. Analysis showed that the components had united with loss of hydrogen chloride, and that little, if any, further decomposition had occurred. The substance may be regarded as the *benzyl- ψ -thiourea ester of isothiohydantoic acid*.

Found: N=18.77; S=20.9.

$C_{11}H_{16}O_2N_2S_2$ requires N=18.6; S=21.3 per cent.

An attempt to prepare the real additive compound by allowing the materials to remain together in cold acetone solution for several days resulted in the isolation of a solid containing Cl=5.7, instead of 10.6 per cent. required by the additive compound.

Thiocarbamide and Methyl monochloroacetate.—Direct addition of these substances was effected by allowing equivalent weights, mixed in acetone solution, to remain for two days. Colourless crystals, which decomposed at 200°, separated from the solution. The crystals readily dissolved in water and gave a strongly acid solution. The *picrate* decomposes at 175°. When the compound was heated with an alkaline solution of lead acetate, no trace of mercaptide was observed, but lead sulphide formed readily. Silver nitrate gave a white precipitate which was soluble in ammonium hydroxide. The ammoniacal solution did not yield mercaptide or sulphide when heated, thus indicating the formation of a silver compound of *isothiohydantoic acid*. A purple coloration in Andreasch's test proved the presence of the group $\cdot CO \cdot CH_2 \cdot S \cdot$. Hence the compound is the *hydrochloride of methyl isothiohydantoate*.

Found: Cl=19.4.

$C_4H_9O_2N_2ClS$ requires Cl=19.2 per cent.

On boiling with alcohol, it was hydrolysed to the hydrochloride of *isothiohydantoic acid* (Found: Cl=23.28. Calc.: Cl=22.86 per cent.). When rather less than one equivalent of sodium hydroxide was added to an aqueous solution of the original compound, prisms, recognised as *isothiohydantoin* (Found: S=27.39. Calc.: S=27.58 per cent.), separated from solution. The substance decomposed at 220°.

Thiocarbamide and Ethyl monochloroacetate.—These substances

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were combined by a similar method to the above. The products separated in glassy, six-sided pyramids which dissolved in water, giving an acid solution. It melts at 107° and decomposes at about 120° .

Found: Cl=17.54.

$C_5H_{11}O_2N_2ClS$ requires Cl=17.63 per cent.

Thiocarbamide methyl dichloroacetate was precipitated on mixing concentrated aqueous solutions of thiocarbamide methyl nitrate and sodium dichloroacetate. White crystals were obtained on crystallising the substance from alcohol. The substance showed all the usual reactions of methyl- ψ -thiourea and none of isothiohydantoin. It decomposes at 165° .

Found: Cl=32.01.

$C_4H_8O_2N_2Cl_2S$ requires Cl=32.4 per cent.

Heating with even deficit of alkali caused the evolution of mercaptan. No sign of further combination was observed after the substance had been heated for several hours in alcoholic solution with thiocarbamide.

Thiocarbamide benzyl dichloroacetate was prepared similarly. No striking peculiarity was observed in its behaviour. It decomposes at 153° .

Found: N=10.2.

$C_{10}H_{12}O_2N_2Cl_2S$ requires N=9.6 per cent.

Thiocarbamide methyl trichloroacetate crystallised in shining leaflets on mixing aqueous solutions of thiocarbamide methyl sulphate and sodium trichloroacetate. Its behaviour was that of an ordinary salt of methyl- ψ -thiourea. Heating with pyridine caused complete decomposition, and on being heated alone it decomposed at 187° . One hundred parts of the substance gave 124.2 parts of silver, whereas 100 parts of $C_4H_8O_2N_2Cl_3S$ require 127.4 parts of silver.

Thiocarbamide benzyl trichloroacetate was prepared similarly. It resembled the preceding compound in appearance and behaviour and decomposed at 150° . An identical product was obtained by heating together benzyl- ψ -thiourea and trichloroacetic acid.

Found: N=8.52; Cl=31.4.

$C_{10}H_{11}O_2N_2Cl_3S$ requires N=8.45; Cl=32.3 per cent.

Alcoholic solutions of this compound were heated for several hours with one, two, and three equivalents, respectively, of thiocarbamide, but no indication of the formation of isothiohydantoin

HEYROVSKÝ: ELECTROAFFINITY OF ALUMINIUM. PART I. 11

derivatives was observed. The residue, from the evaporation of the alcoholic solution also failed to indicate the presence of isothiohydantoin, but reacted freely for ψ -thiourea.

THE CHEMISTRY DEPARTMENT,
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III.—*The Electroaffinity of Aluminium. Part I.* *The Ionisation and Hydrolysis of Aluminium Chloride.*

By JAROSLAV HEYROVSKÝ.

ALUMINIUM chloride is a quaternary, strong electrolyte exerting a fourfold osmotic pressure in dilute solutions. In a solution there may exist the ions AlCl_2^+ , AlCl^+ , Al^{+++} , and Cl^- . There is no evidence for the existence of complexes, such as $(\text{AlCl}_3)_2$; the single molecules seem to possess more affinity for water than for each other.

The cations combine to a certain degree with the hydroxyl ions to form AlCl_2OH , $\text{AlCl}(\text{OH})_2$, and $\text{Al}(\text{OH})_3$; as, however, this hydrolysis does not exceed 3.8 per cent. even in the most dilute solutions concerned, it will first be neglected in considering the dissociation of aluminium chloride.

Let the concentration of aluminium chloride in gram-equivalents per litre be denoted by c , and that of the chloridions resulting from the dissociation be cx (where x is less than 1).

Let the concentration of the Al^{+++} cations, expressed in gram-equivalents per litre, be

$$\begin{aligned} \text{further let } [\text{Al}^{+++}] &= c \cdot y_3 \ (y_3 < \frac{1}{3}), \\ [\text{AlCl}^+] &= c \cdot y_2 \ (y_2 < \frac{2}{3}) \\ [\text{AlCl}_2^+] &= c \cdot y_1 \ (y_1 < \frac{2}{3}) \\ \text{and } [\text{AlCl}_3] &= c \cdot y_0 \ (y_0 < \frac{1}{3}). \end{aligned}$$

$$\begin{aligned} \text{Then } y_0 + y_1 + y_2 + y_3 &= \frac{1}{3} \quad \dots \dots \dots (1) \\ y_1 + 2y_2 + 3y_3 &= x \quad \dots \dots \dots (2) \end{aligned}$$

We shall first consider how the dissociation would change with dilution if the law of mass action were valid.

$$\begin{aligned} \text{We should have: } cy_0 &= K_0 \cdot cy_1 \cdot cx \\ cy_1 &= K_1 \cdot cy_2 \cdot cx \\ cy_2 &= K_2 \cdot cy_3 \cdot cx \end{aligned} \quad \dots \dots \dots (3)$$

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which gives

$$\begin{aligned}y_2 &= K_2 \cdot cx \cdot y_3 \\y_1 &= K_1 K_2 \cdot (cx)^2 \cdot y_3 \\y_0 &= K_0 K_1 K_2 \cdot (cx)^3 \cdot y_3.\end{aligned}$$

Substituting in equation (1), we get

$$y_3 \{ K_0 K_1 K_2 (cx)^3 + K_1 K_2 (cx)^2 + K_2 cx + 1 \} = \frac{1}{3}$$

$$\text{hence } y_3 = \frac{1}{3 \{ K_0 K_1 K_2 (cx)^3 + K_1 K_2 (cx)^2 + K_2 (cx) + 1 \}} = \frac{1}{3a}.$$

Similarly

$$y_2 = \frac{1}{3} \cdot \frac{K_2 (cx)}{a},$$

$$y_1 = \frac{1}{3} \cdot \frac{K_1 K_2 (cx)^2}{a},$$

$$y_0 = \frac{1}{3} \cdot \frac{K_0 K_1 K_2 (cx)^3}{a}.$$

Since

$$x = y_1 + 2y_2 + 3y_3 \quad (2)$$

when c becomes great, x approaches zero, and therefore

y_1 approaches zero

y_2 " "

y_3 " "

And from (1), y_0 approaches $\frac{1}{3}$ (a maximum).

As c approaches zero, x approaches unity; it therefore follows from the above equations that y_3 approaches $\frac{1}{3}$ (a maximum), y_1 , y_2 , and y_0 approach zero.

We can find the maximum values of y_1 and y_2 as follows:

$$y_2 = \frac{1}{3} \cdot \frac{K_2 (cx)}{a}.$$

Therefore

$$\begin{aligned}\frac{dy_2}{d(cx)} &= \frac{K_2}{3a^2} \cdot [-2K_0 K_1 K_2 (cx)^3 - K_1 K_2 (cx)^2 + 1] \\&= \frac{K_2}{3a^2 y_3} \left(-2y_0 - y_1 + y_3 \right) \\&= \frac{K_2}{3a^2 y_3} \left(x - \frac{2}{3} \right).\end{aligned}$$

By equating to zero, we find that y_2 is a maximum when $x = \frac{2}{3}$. Similarly, we may show that

$$\frac{dy_1}{d(cx)} = \frac{K_1 K_2 cx}{3a^2 y_3} \left(x - \frac{1}{3} \right),$$

and therefore y_1 is a maximum when $x = \frac{1}{3}$.

Summing up,

y_0 is a maximum when c is great and x is small, and a minimum when c is very small and $x=1$.

y_1 is a maximum when $x = \frac{1}{3}$ and a minimum when c is very great or very small, that is, when $x = 0$ or $x = 1$.

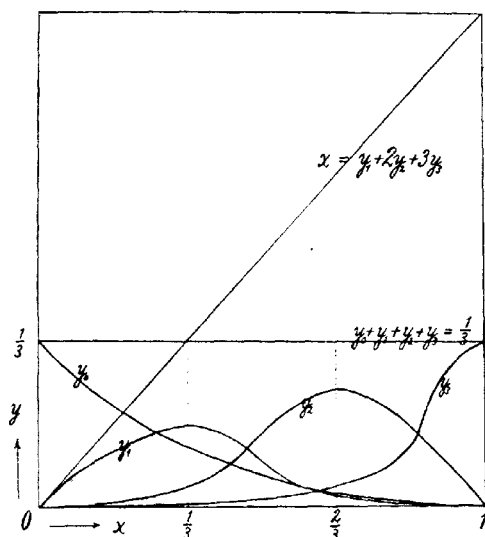
y_2 is a maximum when $x = \frac{2}{3}$ and a minimum when c is very great or very small, that is, when $x = 0$ or $x = 1$.

y_3 is a maximum when c is very small, that is, when $x = 1$, and a minimum when c is very great, that is, when $x = 0$.

The changes of y_1 , y_2 , y_3 , and x , corresponding with the gradual splitting into simpler ions on dilution, are plotted in Fig. 1.

This was deduced for an ideal electrolyte obeying the law of

FIG. 1.



mass action. It can, however, be shown that the same mode of dissociation takes place as indicated in Fig. 1 whatever the law may be so long as it is of the general form

$$\frac{c_{\text{cation}}^a \times c_{\text{anion}}^b}{c_{\text{molecule}}^p} = K.$$

(For van't Hoff's constant, $a = b = \frac{2}{3}p$; for Ostwald's, $a = b = p$.)

Thus, assuming that the indices a , b , c , . . . are in arithmetic progression, we obtain

$$\frac{dy_1}{d(cx)} = d \frac{a+1}{d(cx)} \cdot (cy_2)^m \cdot \frac{c}{3a^2 (cy_2)^{m+1} (cx)^{a+1} (x - \frac{2}{3})},$$

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which means that y_2 is a maximum when $x = \frac{2}{3}$, just as in the previous case, and similarly for y_1 and y_3 .

The coefficient x , representing the ionised fraction of chlorine, may be determined from the potential of a calomel electrode filled with the respective aluminium chloride solution.

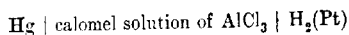
These results, however, would give only the maximal and minimal value of y_3 , that is, of the dissociation into Al^{+++} ions, but no evaluation whatever as to y_1 and y_2 .

Further conclusions respecting the $[\text{Al}^{+++}]$ concentration can be drawn from the hydrolysis of aluminium chloride solutions when solid aluminium hydroxide is present. Then $[\text{Al}^{+++}] \cdot [\text{OH}']^3 = K$, the concentration of $[\text{OH}']$ being determinable by the potential of a hydrogen electrode.

To evaluate the remaining ionic concentrations, specific conductivities of aluminium chloride solutions must be considered.

Measurements of Electromotive Force.

Measurements of cells of the type



were made with all precautions in the manner described by Tolman and Ferguson (*J. Amer. Chem. Soc.*, 1912, **34**, 232) and Acree (*Amer. Chem. J.*, 1911, **46**, 585, 621, 638), using platinised glass electrodes. Readings on the potentiometer could be made to a tenth of a millivolt.

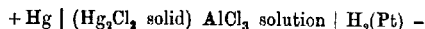
In order to examine the reproducibility of the electrodes used, the cell was filled with 0.100 N-hydrochloric acid. The *E.M.F.* at 18° and 760 mm. was found to be constant for three days at 0.3958 ± 0.0003 volt.

The mercury used was purified and twice redistilled. The hydrogen was passed through alkaline permanganate and lead nitrate solutions, and was finally bubbled through the same solution as was being measured in the cell.

The aluminium chloride was purified by precipitation three times from solution by means of hydrogen chloride, and the solutions were kept at 25° in bottles, the corks of which were covered with paraffin.

The cell was kept in a thermostat at 25°, and the readings were repeated after three or four weeks. The effect of barometric change was much less than the variations due to experimental errors, which became appreciable in dilute solutions. Two hydrogen electrodes were used simultaneously dipping into the same solution; they did not differ by more than 0.5 millivolt.

In this way, the following results were obtained for the cell:



Concentration of AlCl_3 in gram-equiv. per litre.	<i>E.M.F.</i> observed at different times.				Mean <i>E.M.F.</i> in volt.
2.29	0.3739, 0.3735	0.3725, 0.3725			0.373
0.368	0.4810, 0.4810	0.4808, 0.4807			0.481
0.0184	0.6000, 0.6005	0.5930, 0.5924			0.595
0.0092	0.6190, 0.6186	0.6170	—		0.618
0.00613	0.632	—	0.634	—	0.633
0.0046	0.639, 0.646	0.643, 0.641			0.643
0.00306	0.659, 0.658	0.661, 0.655			0.658

In other experiments, the aluminium chloride solutions were shaken with precipitated aluminium hydroxide for several weeks previous to being introduced into the cell. With these solutions, the following results were obtained:

Concentration of AlCl_3 solutions in gram-equiv. per litre.	<i>E.M.F.</i> observed at different times.				Mean <i>E.M.F.</i> in volt.
2.88	0.4221, 0.4225	0.4218	—		0.4222
0.934	0.4940, 0.4934	0.4939, 0.4934			0.4937
0.1845	0.5351	0.5359			0.5355
0.0675	0.5623	0.5614			0.5620
0.0337	0.5804	0.5818, 0.5807			0.5813
0.02134	0.5965, 0.5980	0.5981, 0.5996			0.5984
0.01067	0.6147, 0.6158				0.6150
0.00675	0.6376	—	0.6360, 0.632		0.635
0.00213	0.6685	—	0.6667		0.668

In order to find the potentials of the single electrodes, the aluminium chloride-calomel electrodes were compared with normal and tenth-normal calomel electrodes at 25°. Saturated, half-saturated, and quarter-saturated potassium chloride solutions were used successively as intermediate solutions and the values extrapolated. This method of eliminating the liquid potential was found to be much more trustworthy than the use of potassium nitrate or ammonium nitrate solutions. All glass tubes were at least 0.5 cm. wide, and no glass taps were used.

The following values were found for the potential π_N of the electrode.

$\text{Hg} \mid (\text{Hg}_2\text{Cl}_2) \mid \text{AlCl}_3 \text{ solution}$, taking the normal calomel electrode as zero:

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Quarter, half, and fully saturated potassium chloride solution as intermediate solution.

Concentration of AlCl_3 .	P.D. against N-calomel electrode.			P.D. against N/10-calomel electrode.			π_N extrapolated.
2.29	-0.0090,	-0.0114,	-0.0137	-0.0615,	-0.0625,	-0.0664	-0.0140
0.368	+0.0294,	0.0282,	0.0278	-0.0249,	-0.0252,	-0.0267	+0.0273
0.0409	0.0766,	0.0768,	0.0772	+0.0238,	0.0238,	0.0234	+0.0772
0.0184	0.0970,	0.0976,	0.0978	0.0444,	0.0444,	0.0444	+0.0985
0.0092	0.1174,	0.1168,	0.1155	0.0636,	0.0634,	0.0633	+0.1150
0.00613	0.1257,	0.1255,	0.1253	0.0721	—	—	+0.1250
0.00460	0.1352,	0.1328,	0.1320	—	—	—	+0.1320
0.00306	—	0.1420,	0.1420	0.0868,	0.0870,	0.0880	+0.1420

Similarly, the values of π_N of calomel electrodes filled with aluminium chloride solutions saturated with aluminium hydroxide were obtained:

Concentration of AlCl_3 .	P.D. against N-calomel electrode using quarter, half, and fully saturated potassium chloride solution.			π_N extrapolated.
2.88	-0.0105,	-0.0132,	-0.015	-0.017
0.934	+0.0106,	0.0092,	0.0076	+0.007
0.0675	+0.0721,	0.0720,	0.0710	+0.070
0.00675	+0.1185,	0.1180,	0.1172	+0.117

For the calculations of conductivities, Jones' data (*Carnegie Inst. Publ.*, No. 170), which agree with those of Ley (*Zeitsch. physikal. Chem.*, 1899, **30**, 206), were used.

Molecular conductivity at 25°.	Dilution v 1 mol. in v litres.	Molecular conductivity at 25°.	Dilution v 1 mol. in v litres.
193.51	4	341.24	512
220.86	8	360.56	1024
265.12	32	381.44	2048
308.80	128	398.79	4096

Calculation of Dissociation.

The single potentials, π_N , were plotted against $\log c$, and the values of π_N for use in the following calculations were taken from the smooth curve.

The concentrations of chloridions were found in the following way. If π_N were the potential of a calomel electrode in a given aluminium chloride solution, then the concentration of a potassium chloride solution in which the calomel electrode had this same potential, π_N , was found from the curve showing the relation between the potential of a calomel electrode and the logarithm of the concentration of potassium chloride. It was assumed that the concentration of chloridions in these two solutions was the same.

and the absolute value of the chloridion concentration was then calculated from measurements of the conductivity of potassium chloride solution. The following values of π_N for calomel electrodes in potassium chloride solutions were used (Abegg, Auerbach, and Luther, *Abhandl. Bunsen Ges.*, No. 5):

π_N of N-	calomel electrode at 25° = 0.000	volt
" N/10-	" " "	0.0541
" N/100-	" " "	0.1087
" N/1000-	" " "	0.164

Column 3 (table I) was calculated in this way. From this, the ratio $\frac{[Cl']}{c} = x$, column 4, was obtained.

For example, in an 0.0092*N*-solution of aluminium chloride the potential of a calomel electrode is equal to the potential of a calomel electrode in potassium chloride solution, for which $\log c = 3.9114$, that is, 0.008155*N*. This, being ionised to the extent of 94.6 per cent., has $[Cl'] = 0.007715$, which must be identical with the concentration of chlorine ions in an 0.0092*N*-solution of aluminium chloride. Hence $x = \frac{[Cl']}{C} = 0.8381$.

The $[Cl']$ was not calculated directly from the formula

$$\pi = -0.0591 \log_{10}[Cl'],$$

because second-class (anionic) electrode potentials do not agree exactly with the values calculated from conductivity data, possibly due to the formation of complex mercury ions.

Hydrogen electrode potentials, however, were found to vary strictly according to the formula $\pi = -0.0591 \log_{10} C_H$, when the concentration of hydrogen ions, C_H , is determined from conductivity (Bjerrum, *Zeitsch. physikal. Chem.*, 1905, **53**, 428; 1907, **59**, 341).

Thus column 7 (table I) was calculated from the potential of hydrogen electrode, π_H (referred to the normal potassium chloride-calomel electrode as zero), the difference of the two normal electrodes having been taken as 0.2837 volt.

The ratio, $\frac{C_N}{c}$ (column 8), shows the degree of hydrolysis, h .

For example, the potential of a hydrogen electrode in 0.0092*N*-aluminium chloride solution is -0.5037 volt.

TABLE I.

1	2	3	4	5	6	7	8	9
c = con- centration of AlCl_3 in gram- equivalent per litre.	$\log_{10} c$.	$[\text{Cl}']$.	x .	x' .	π_{H} in volt.	$[\text{H}']$.	$[\text{H}']$ c	Maxi- mum y_0 .
0.00306	3.48572	0.00267	0.873	0.835	0.5162	0.000116	0.0378	0.635
0.00460	3.66276	0.00395	0.859	0.829	0.5118	0.000138	0.0390	0.657
0.00613	3.78746	0.00522	0.851	0.825	0.5080	0.0001603	0.0262	0.658
0.00920	3.96400	0.00772	0.838	0.817	0.5037	0.0001897	0.0206	0.661
0.01585	5.2000	0.01295	0.817	0.803	0.4980	0.0002275	0.0143	0.665
0.02291	5.3600	0.01848	0.806	0.794	0.4937	0.000280	0.0122	0.667
0.03162	2.5000	0.0251	0.793	0.783	0.4900	0.000323	0.0102	0.672
0.05012	2.7000	0.0387	0.772	0.764	0.4850	0.000393	0.00783	0.678
0.1585	1.2000	0.1149	0.725	0.721	0.4710	0.000659	0.0042	0.693
0.480	1.6810	—	0.666	0.664	—	—	0.00362	0.112
0.631	1.800	—	—	0.646	—	—	0.00360	—
1.2359	0.092	0.7550	0.611	0.607	0.4190	0.00520	0.00421	0.131
2.290	0.3598	1.310	0.572	0.564	0.3870	0.01807	0.00789	0.145

Hence $0.0591 \log_{10} C_{\text{H}'} = -0.5037 + 0.2837 = -0.2200$ volt

$$\log_{10} C_{\text{H}'} = -\frac{0.2200}{0.0591} = -3.722 = 4.278$$

from which $C_{\text{H}'} = 0.0001897$

$$h = \frac{C_{\text{H}'}}{c} = 0.0206 = 2.06 \text{ per cent.}$$

As the hydrolysis in the solutions used is less than 3.8 per cent., we may neglect the concentrations of cations such as $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})^{++}$, and assume

$$[\text{Al}^{+++}] + [\text{AlCl}^{++}] + [\text{AlCl}_2^+] + [\text{H}'] = [\text{Cl}'],$$

or

$$3cy_3 + 2cy_2 + cy_1 + C_{\text{H}'} = cx,$$

from which it follows that

$$3y_3 + 2y_2 + y_1 = x - h = x'.$$

The values of x' (column 5) are obtained by subtracting the numbers in column 8 from those in column 4.

This number, x' , limits the value of y_3 , the maximum value of which can be $\frac{x'}{3}$ (when no other cations exist in solution, in which case, also, y_0 is at a maximum). The minimal value of y_3 is $x' - \frac{2}{3}$ in the case when most of the AlCl^{++} cations are formed. In this way, columns 9, 10, and 11 were obtained.

Considering the difficulty with which second and third ionic charges are acquired, the minimal values of y_3 are more probable.

TABLE I.

10	11	12	13	14	15	16	17	18	19	20
		Equi- valent con- duc- tivity.		A	π_H'		a_{H^+} $[H^+]^0$			
y_2	y_3	λ_e	A	x'	in volt.	$[H]$	$[H]^0$	y_2	y_3	y_1
0.278	0.168	120.2	40.9	49.0	as π_H	as $[H]$	1	0.180	0.142	0.01
0.276	0.162	116.3	40.7	49.3	—	—	—	0.175*	0.153*	—
0.275	0.158	113.7	40.5	48.93	—	—	—	0.170*	0.161*	—
0.272	0.150	110.3	40.0	48.74	—	—	—	0.160*	0.169*	—
0.268	0.136	106.0	39.0	49.18	0.503	0.000187	0.811	0.146	0.178	0.009
0.265	0.127	103.0	38.1	47.88	0.4985	0.000207	0.761	0.137	0.187	0.009
0.261	0.116	100.0	36.9	46.8	0.498	0.000227	0.727	0.131	0.188	0.014
0.255	0.097	95.3	34.5	45.18	0.4955	0.000260	0.684	0.123	0.19	—
0.240	0.054	83.3	27.5	38.14	0.490	0.000323	0.418	0.075	0.2	0.10
0.221	0	—	—	—	0.487	0.000392	0.248	0.044	0.2	0.13
—	—	—	—	—	—	—	—	—	—	—
0.202	0	—	—	—	—	—	—	—	—	—
0.188	0	—	—	—	—	—	—	—	—	—

* Those values are found by extrapolation.

In order to obtain more precise numbers, conductivity results have to be included. Denoting by M_1 , M_2 , M_3 the mobilities of cations carrying the total charge of one faraday each, that is, of the ions $AlCl_2^+$, $\frac{1}{2}AlCl^+$, $\frac{1}{3}Al^{+++}$ respectively, and taking the mobilities of chloridion as 75.0 and that of hydriion as 365.0 at 25°, the equivalent conductivity of a solution of aluminium chloride, λ_e , is

$$\lambda_e = 3y_3M_3 + 2y_2M_2 + y_1M_1 + x \cdot 75 + h \cdot 365,$$

from which A is obtained (column 13), as

$$A = 3y_3M_3 + 2y_2M_2 + y_1M_1 - \lambda_e - x \cdot 75 - h \cdot 365.$$

The total charge carried by the three different cations $AlCl_2^+$, $AlCl^+$, and Al^{+++} is cx' faradays, and as they contribute to the conductivity, the amount A , the mean equivalent mobility for one cation is $\frac{A}{x'}$. Since this value, as is evident from column 14, approaches 49.2 as the solution becomes very dilute and all the cations become Al^{+++} , the number 49.2 has been taken as the most probable equivalent mobility of Al^{+++} .

In order to evaluate the other unknowns, more relations are necessary. These are obtained from the most dilute solutions where the third stage of hydrolysis is reached, and are supposed to be in equilibrium with solid aluminium hydroxide, the values of π_H in pure aluminium chloride solutions and in those saturated

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with aluminium hydroxide (column 15) coinciding in concentrations less than 0.01*N*. In these solutions,

$$[\text{OH}']^3 \cdot cy_3 = K_{\text{Al}(\text{OH})_3}$$

where $K_{\text{Al}(\text{OH})_3}$ denotes the ionic product of aluminium hydroxide. Its value lies, according to the values of y_3 , between 1.0 and 1.5×10^{-33} (the ionic product of water being taken as 10^{-14}).

Further, in most dilute solutions y_0 is negligible, so that

$$y_1 + y_2 + y_3 = \frac{1}{3}.$$

Solving these equations for the three most dilute solutions, we get

$$K_{\text{Al}(\text{OH})_3} = 1.06 \times 10^{-33} \quad M_2 = 47.0.$$

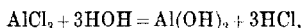
$$M_3 = \text{about } 30,$$

and the different values of y_1 , y_2 , and y_3 are given in columns 18, 19, 20.

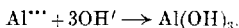
The values of y_3 in concentrations greater than 0.01*N* were calculated from the ratio of hydron concentrations $[\text{H}']'$ in solutions of aluminium chloride saturated with aluminium hydroxide to $[\text{H}']$ in solutions of aluminium chloride alone. In column 17 a denotes the ratio of the cube of $[\text{H}']'$ obtained from the potential π_{H}' of the hydrogen electrode in these solutions to the cube of $[\text{H}']$ in aluminium chloride solutions.

Conclusions.

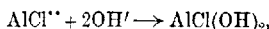
Progressive Hydrolysis.—In solutions below 0.01*N*, the third stage of hydrolysis exists,



or the ionic reaction



For the second stage, having the ionic reaction



the expression

$$\frac{cy_2 \cdot K_w^2}{[\text{H}']^2 \cdot [\text{AlCl}(\text{OH})_2]'}$$

should be constant. Here K_w denotes the ionic product of water.

Similarly for the first stage, the expression

$$\frac{cy_1 \cdot K_w}{[\text{H}'] \cdot [\text{AlCl}_2\text{OH}]}$$

should be constant.

These relations cannot, however, be tested, as the concentrations of $\text{AlCl}(\text{OH})_2$ and AlCl_2OH are not known with sufficient accuracy.

Since the base AlCl_2OH containing two chlorine atoms is prob

ably weaker than the base $\text{AlCl}(\text{OH})_2$ having one more chlorine atom in place of hydroxyl, the slight increase of hydrolysis in the most concentrated solutions (minimum in 0.5*N*-aluminium chloride solution; see Fig. 2) might be interpreted as due to first-stage hydrolysis.

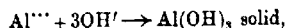
A similar minimum of hydrolysis in the most concentrated solutions was found by Kablukov and Sachanov (*Zeitsch. physikal. Chem.*, 1909, **69**, 419) in the hydrolysis of aluminium bromide at 25° and by Bruner (*Zeitsch. physikal. Chem.*, 1900, **32**, 133) in the hydrolysis of aluminium chloride at 40°.

The determination of hydrolysis by means of hydrogen electrode potentials has been made by Denham (T., 1908, **93**, 41), who obtained for aluminium chloride solutions ranging from 0.19 to 0.024*N*, values of the potential of the electrode about 20 millivolts lower than those observed by the author. He therefore found three times more hydrolysis. In his experiments, the liquid potential was eliminated by means of a concentrated solution of ammonium nitrate, the solutions being allowed twenty-four hours to come to equilibrium.

The hydrolysis of aluminium salts seems to be influenced by the mode of dissolution. For example, if the solution is raised to a temperature above 25°, it does not necessarily return to the same condition at 25° as it was before (Jones, *loc. cit.*). Moreover, a slight excess of hydrochloric acid in the dry salt would cause too great an acidity, and any adjustment of the equilibrium takes place very slowly. This difficulty in attaining equilibrium, if once disturbed, seems to be due to the presence of colloidal aluminium hydroxide, which exhibits the phenomenon of ageing, showing marked insolubility when not in the nascent state. The solutions must be therefore prepared and kept so far as possible at the same temperature. Kablukov and Sachanov's results (*loc. cit.*) for the hydrolysis (at 25°) of aluminium bromide, calculated from *E.M.F.* measurements, are very close to the values given in this paper.

The Heat of Ionisation of Aluminium Hydroxide.—Kulgren (*Zeitsch. physikal. Chem.*, 1913, **85**, 466) measured very accurately the hydrolysis of aluminium chloride at 85° and 100°. From his results, and from the values given in Fig. 2 (curve *h*), the heat of ionisation of aluminium hydroxide can be obtained in the following way.

The degree of hydrolysis of aluminium chloride at the dilution $\tau=512$ is 4.7 per cent. at 25°, 34.09 per cent. at 85°, and 47.68 per cent. at 100°. Since at this dilution the third stage of hydrolysis exists, the heat of ionisation of the reaction,



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can be calculated from the data given above by means of van't Hoff's isochore.

Thus, considering the equilibria at two temperatures, T and T' ,

$$\frac{[\text{Al}(\text{OH})_3] \cdot K}{[\text{Al}(\text{OH})_3]' \cdot K'} = \frac{[\text{Al}'''] \cdot [\text{OH}]^3}{[\text{Al}''']' \cdot [\text{OH}]^3} = \frac{[\text{Al}'''] \cdot K_w^3 \cdot [\text{H}]^3}{[\text{Al}''']' \cdot K_w'^3 \cdot [\text{H}]^3}$$

Further, at the same dilution, $v=512$, the concentrations of the Al''' ions can be taken as equal to the non-hydrolysed portion in solution, and since at this great dilution some solid aluminium hydroxide will certainly have separated out, we can write:

$$\frac{[\text{Al}(\text{OH})_3] \cdot K}{[\text{Al}(\text{OH})_3]' \cdot K'} = \frac{K_{\text{Al}(\text{OH})_3}}{K'_{\text{Al}(\text{OH})_3}} = \frac{1-h}{1-h'} \cdot \frac{K_w^3}{K_w'^3} \cdot \frac{h^3}{h'^3}$$

where h denotes the fraction hydrolysed and $K_{\text{Al}(\text{OH})_3}$ and $K'_{\text{Al}(\text{OH})_3}$ are the solubility products. Substituting in van't Hoff's formula, we get:

$$Q = R \frac{T \cdot T'}{T - T'} \log \frac{1-h}{1-h'} \cdot \frac{K_w^3}{K_w'^3} \cdot \frac{h^3}{h'^3}$$

Taking K_w at $100^\circ = 48 \times 10^{-14}$, at $85^\circ = 27.6 \times 10^{-14}$, and at $25^\circ = 1 \times 10^{-14}$, as extrapolated from Noyes' numbers (*Zeitsch. physikal. Chem.*, 1910, **73**, 1), we obtain:

$$Q \text{ between } 25^\circ \text{ and } 100^\circ = 11970 \text{ cal.},$$

$$Q \text{ „ } 25^\circ \text{ „ } 85^\circ = 12860 \text{ cal.}$$

Thus the heat of ionisation of one gram-molecule of solid aluminium hydroxide into the ions Al''' and OH' is about 12000 cal.

When neutralised by strong acids, one equivalent of aluminium hydroxide should evolve 13700 calories less than the heat necessary to ionise the molecule, that is,

$$13700 - 4133 = 9567 \text{ cal.}$$

Thomsen found 9320 cal., which agrees with the calculated value, indicating a base of medium strength.

The Diffusion Potential.

Having found the ionic concentrations and the corresponding mobilities, it seemed interesting to compare the potential differences observed on liquid boundaries between single aluminium chloride solutions with the values calculated from Henderson's formula (*Zeitsch. physikal. Chem.*, 1908, **63**, 325). The formula for the diffusion potential E is

$$E = \frac{RT}{F} \cdot \frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1' + V_1') - (U_2' + V_2')} \log_e \frac{U_1' + V_1'}{U_2' + V_2'}$$

where

$$\begin{aligned} U_1 &= u_1 c_1 + u_2 c_2 + \dots & V_1 &= v_1 c_1 + v_2 c_2 + \dots \\ U_1' &= u_1 c_1 w_1 + u_2 c_2 w_2 + \dots & V_1' &= v_1 c_1 w_1 + v_2 c_2 w_2 + \dots \end{aligned}$$

c, \bar{c} denoting concentrations of cation and anion,
 u, \bar{v} „ equivalent mobilities of cation and anion,
 w, \bar{w} „ valencies of cation and anion respectively.

In the special case of aluminium chloride,

$$V_1 = V_1' = M_{Cl} \cdot cx = 75 \cdot cx.$$

$$U_1 + V_1 = K_c \text{ (specific conductivity), therefore } U_1 = K_c - 75 \cdot cx.$$

$$U_1 - V_1 = K_c - 150 \cdot cx = c(\lambda_c - 150x).$$

Further, neglecting the hydrolysis,

$$U_1 = c(y_1 M_1 + y_2 \cdot 2M_2 + y_3 \cdot 3M_3)$$

$$U_1' = c(y_1 M_1 + 2y_2 \cdot 2M_2 + 3y_3 \cdot 3M_3)$$

$$\text{hence } U_1' - U_1 = c(2y_2 M_2 + 6y_3 M_3)$$

$$\text{further } U_1' + V_1' = c(2y_2 M_2 + 6y_3 M_3) + U_1 + V_1$$

$$= c(\lambda_c + 2y_2 M_2 + 6y_3 M_3).$$

Finally,

$$\begin{aligned}
 \beta = 0.059 \frac{c(\lambda_c - 150x) - c'(\lambda_c' - 150x')}{c(\lambda_c + 2y_2 M_2 + 6y_3 M_3) - c'(\lambda_c' + 2y_2' M_2' + 6y_3' M_3')} \\
 \times \log \frac{c(\lambda_c + 2y_2 M_2 + 6y_3 M_3)}{c'(\lambda_c' + 2y_2' M_2' + 6y_3' M_3')}.
 \end{aligned}$$

TABLE II.

Preliminary Calculations.

Concen- tration of $AlCl_3$ in equiv- alent litres.	λ_c	x	y_2	y_3	$2M_2y_2 + 6M_3y_3$	$\lambda_c + 2M_2y_2 + 6M_3y_3$	$\alpha = c(\lambda_c + 2M_2y_2 + 6M_3y_3) - 150x$	$b = c(\lambda_c + 2M_2y_2 + 6M_3y_3)$
0.1227	85.7	0.730	0.1	0.2	48.4	23.8	134.1	-2.92 16.45
0.0184	104.7	0.814	0.14	0.18	58.3	17.4	163.0	-0.32 2.99
0.0092	110.3	0.838	0.16	0.17	63.4	14.4	173.7	-0.133 1.598
0.0013	113.7	0.851	0.17	0.16	65.3	14.0	179.0	-0.0858 1.097

$$\text{Calculation of } E = 0.059 \frac{a - a'}{b - b'} \log_{10} \frac{b}{b'}, \text{ volts.}$$

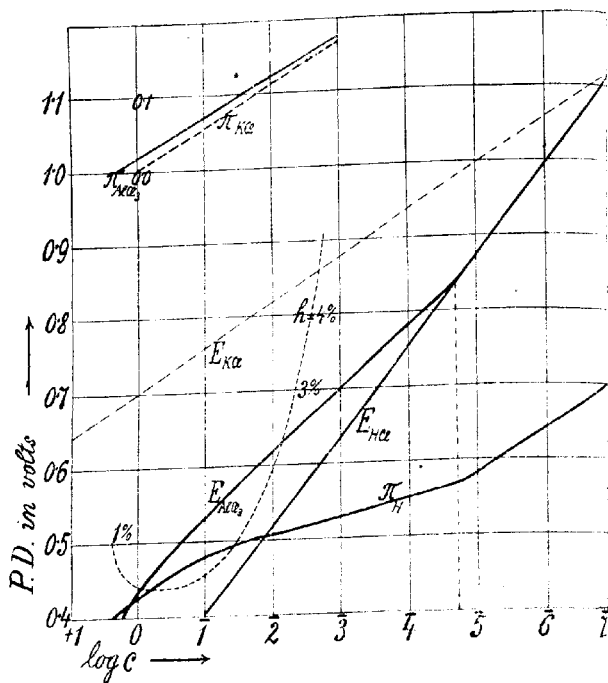
According to Henderson's paper, the $E.M.F.$ is here denoted as positive if the current passes from the first solution to the second side the cell.

E.M.F. measured between calomel electrodes in $AlCl_3$ solutions of concentration.		P.D. of single electrodes.	E.M.F. observed without elimination of diffusion P.D.	E observed.	E calculated.
0.1227	0.0184	0.019	0.0100	—0.009	—0.0084
0.1227	0.0092	0.040	0.0290	—0.011	—0.0112
0.1227	0.00613	0.046	0.0321	—0.014	—0.0128
0.0184	0.092	0.017	0.0153	—0.002	—0.0022
0.0184	0.0613	0.027	0.019	—0.008	—0.0032

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In table II, the potential differences calculated in this way are compared with those directly observed, this being the first instance in which Henderson's formula could be tested in the case of trivalent ions.

FIG. 2.



The Activity of Hydrochloric Acid in Aluminium Chloride Solutions.

The results of E.M.F. measurements are plotted in Fig. 2. The lines marked π_{KCl} and π_{AlCl_3} give the potentials of calomel electrodes in solutions of potassium chloride and aluminium chloride respectively, showing that the activity of chlorine ions in aluminium chloride solutions is very near to that which obtains in equivalent solutions of potassium chloride, the dissociation into chloridions in the case of aluminium chloride being only about 20 per cent. less than in the case of potassium chloride.

The abscissæ in Fig. 2 are in all cases logarithms of the concentration c expressed in gram-equivalents per litre.

The curve $h = \frac{C_H}{c}$ shows the change of hydrolysis with dilution.

The curve π_H represents the potential of the hydrogen electrode in aluminium chloride solutions, referred to the normal calomel electrode as zero (the values to be taken as negative).

The curve E_{AlCl_3} shows the variation of *E.M.F.* of the cell $Hg|calomel, AlCl_3 \text{ solution}|H_2$, giving the activities of chlorine and hydrogen ions, or the activity of hydrochloric acid, according to the formula

$$\begin{aligned} E_{AlCl_3} &= RT \log_e \frac{P_H \cdot P_{Cl}}{[H] \cdot [Cl]} = 0.2837 - 0.0591 \log_{10} [H] \cdot [Cl] \\ &= 0.2837 - 0.1182 \log_{10} [HCl]. \end{aligned}$$

Thus the curve E_{AlCl_3} shows the partial pressures of hydrochloric acid formed by the hydrolysis of aluminium chloride.

If this curve is compared with the curve E_{HCl} , expressing the partial pressure or activity of pure hydrochloric acid solutions as obtained from the results of Tolman and Ferguson (*loc. cit.*), corrected from 18° to 25°, it is possible to find for every aluminium chloride solution the concentration of pure hydrochloric acid, which would have the same activity of hydrogen chloride (exert the same partial pressure).

Thus in 2.29 $N-AlCl_3$ the HCl tension is that of 0.176 $N-HCl$.

1.00	"	"	"	0.0582	"
0.368	"	"	"	0.0184	"
0.100	"	"	"	0.00617	"
0.0184	"	"	"	0.00178	"

the potential difference between calomel and hydrogen electrodes, that is, the ordinate in each pair of solutions being the same.

The values of E_{HCl} for dilute solutions have been obtained by extrapolating from the observed values and assuming that E_H increases by 0.1182 volt for a decrease in concentration of 10:1.

Similarly, the line E_{AlCl_3} was produced in the direction corresponding with the theoretical increase of *E.M.F.* by

$$\frac{RT}{F} \log [H] \cdot [Cl] = \frac{RT}{F} \log [Al^{+++}]^{\frac{1}{3}} \cdot c = \frac{RT}{F} \log c_3^{\frac{1}{3}} = \frac{1}{3} \cdot 0.0591 \text{ volt}$$

for tenfold dilution, which at the highest dilutions will be greater owing to the decrease of Al^{+++} ions due to the precipitation as $Al(OH)_3$.

As is seen in the figure, these lines will meet at a normality of

about 0.000027, where practically total hydrolysis is reached, so that in concentrations less than $10^{-5}N$, aluminium chloride behaves similarly to boron trichloride, which is completely hydrolysed in solution; on the other hand, aluminium hydroxide does not dissolve in $10^{-5}N$ -hydrochloric acid to form aluminium chloride.

The value of π_H at great dilutions has been assumed to be proportional to $\log[H^+]$. From this, the value of π_H in a neutral solution is 0.70 volt.

The line E_{KCl} , representing the activity of hydrochloric acid in solutions of an ideal non-hydrolysable chloride of a strong base, has been drawn, in which π_H is taken as equal to 0.700 volt.

Similar *E.M.F.* curves for chlorides must all lie between the two extremes, namely, E_{KCl} and E_{HCl} lines, the slope becoming steeper as the alkalinity of the metal decreases. Thus a chloride of a strong base like lanthanum trichloride would give a curve very similar to E_{KCl} , whereas boron chloride would give nearly that of E_{HCl} . This would be a precise and distinct way of expressing hydrolysis.

Summary.

(1) From conductivity data and *E.M.F.* measurements of aluminium chloride concentration cells, the amount of ionisation and hydrolysis was determined, and the gradual ionisation of cations calculated.

(2) The ionisation of aluminium chloride into chloridions is about 20 per cent. less than the ionisation of potassium chloride of equivalent concentration.

(3) The basic solubility product of aluminium hydroxide is

$$[Al^{+++}].[OH']^3 = 1.06 \times 10^{-33}.$$

(4) The heat of ionisation of aluminium hydroxide has been calculated.

(5) The mobility of the ion Al^{+++} , 3×49.2 , that of the ion $AlCl^{++} = 2 \times 47$.

(6) Henderson's formula for the diffusion potential between solutions of aluminium chloride has been found to hold good.

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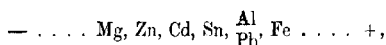
[Received, October 20th, 1919.]

IV.—The Electroaffinity of Aluminium. Part II. The Aluminium Electrode.

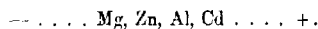
By JAROSLAV HEYROVSKÝ.

Passive Aluminium.

Potentials.—The position of aluminium in the electro-potential series has long remained uncertain. Thus Streinz (*Ber. Wien. Akad.*, 1878, **77**, 410), from measurements in aluminium nitrate solutions, placed aluminium as follows:

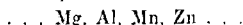


and from measurements in aluminium chloride solutions thus:



Wright and Thompson (*Phil. Mag.*, 1885, [v], **19**, 102, 197) found aluminium to be more positive than zinc in solutions of chlorides by 0.280 volt, of bromides by 0.295 volt, and of sulphates by 0.537 volt, although from thermo-chemical determinations they expected a potential one volt more negative than for zinc.

Neumann (*Zeitsch. physikal. Chem.*, 1894, **14**, 193), using amalgamated aluminium, placed it as follows:



Burgess and Hambuechen (*Electrochem. Ind.*, 1903, **1**, 165) found that the potential of aluminium wires varied from -0.3 to -1.3 volt (referred to the normal hydrogen electrode).

Van Deventer (*Chem. Weekblad*, 1907, **4**, 625, 771) found that amalgamated aluminium had a potential similar to magnesium, whilst the inactive metal was more noble than zinc.

Obviously, in all cases where the metal is not amalgamated, aluminium remains in a passive condition, the passivity being caused by a skin of oxide or hydroxide, as is evident on dissolving aluminium in dilute alkalis or during amalgamation, when the adherent skin peels off.

The potential of metallic aluminium, like that of any passive electrode, is not influenced by the presence of aluminium ions in solution. The metal behaves rather as a gas electrode, being sensitive to oxidising and reducing agents, besides being influenced by anions (compare Jory and Barnes, *Trans. Amer. Electrochem. Soc.*, 1903, **3**, 95). Great sensitivity to shocks was also observed. The following table of experimental results shows the passivity of aluminium wire:

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Cell (at room temperature), first electrode is +.	Behaviour.	Observed <i>E.M.F.</i> in volts.
Hg calomel <i>N</i> -KCl soln. Al	Showing sudden changes and great fluctuations of <i>E.M.F.</i>	0.77—1.67
Hg calomel <i>N</i> /10-KCl soln. Al	When not moved	0.76—0.80
	Immediately after the aluminium surface has been rubbed on glass fragments.	1.40—1.47
	Allowed to remain.	< 1.0
	Again rubbed.	1.48
	Current of oxygen passed round the electrode.	0.6—0.7 (least observed <i>E.M.F.</i>)
	Current of hydrogen passed.	1.38

The potential is most negative in solutions of chlorides; it is less negative in bromides, iodides, sulphates, and most passive in nitrate solutions. Evidently solutions of compounds of a more oxidising character passivify aluminium more intensively. This is in accordance with the known fact (compare Müller, *Zeitsch. physikal. Chem.*, 1909, **69**, 481) that the passivifying influence of an anion is inversely proportional to the solubility of the product formed at the electrode (that is, the oxide).

Dissolution of Metallic Aluminium.—The combined action of the active cation H^+ and the anions Cl^- , Br^- , and I^- activates aluminium so that it decomposes water, evolving hydrogen even in the dilute acids. Centnerszwer and Sachs (*Zeitsch. physikal. Chem.*, 1914, **87**, 692) found that the rate of evolution of hydrogen in *N*-hydrochloric acid was 0.066 c.c. per sq. cm. per minute, in *N*-hydrobromic acid 0.002 c.c., and in hydriodic acid still less. The dissolution in *N*-sulphuric acid was much slower, whereas in nitric acid no hydrogen was evolved.

The following experiments were made at the ordinary temperature:

Acid used.	Evolution of hydrogen.	Notes.
Sulphuric acid <i>N</i> /10.	None.	But solutions in contact with metal for some days were found to contain aluminium salt.
" <i>N</i> .	Slow.	—
" concentrated.	Slow.	Yellowish or orange coating of sulphur deposits on metal.
Nitric acid, dilute or concentrated.	None.	Solutions were found to contain aluminium salt. If some chloride is added, bubbles are evolved at once.
Hydrochloric acid, dilute or concentrated.	Strong.	If potassium chlorate is added, evolution increases.
Sulphurous acid.	Moderate.	Odour of hydrogen sulphide.

Acid used.	Evolution of hydrogen.	Notes.
Organic acids.	None.	Insoluble.
Potassium iodide and iodine solution.	Slow.	—
Potassium, sodium or barium hydroxides, dilute or concentrated.	Strong.	Concentrated ammonia and potassium carbonate solutions also dissolve the metal.

The dissolution in pure concentrated sulphuric acid is interesting. If we suppose that electrochemical processes cause corrosion, then the precipitation of sulphur on aluminium must be regarded as cathodic deposition, the few cations, S^{+} , which might exist in minute quantities in concentrated sulphuric acid being thrown down as a more noble element with less solution tension than aluminium.

Electro-deposition of Metals by Aluminium.—Similarly, the deposition of any other more noble metal on aluminium is influenced by anions present in solution, as they determine the potential of the metallic aluminium.

In this connexion, the following results were obtained:

Solution into which aluminium is dipped.	Deposition of metal.	Evolution of hydrogen.	Notes.
Gold chloride, dilute.	Gold deposits at once.	Strong.	Solution turns violet.
Mercuric chloride, dilute.	Instantly amalgamated.	Strong.	—
Mercurous chloride.	Slow amalgamation.	Slow.	Mercurous chloride must be in contact with metal.
Solution of mercuric oxide in nitric acid.	No action.	—	If trace of chloride is added, amalgamation occurs.
Silver nitrate, dilute or concentrated.	Fine crystals of silver.	None.	—
Cupric chloride, cupric bromide, cupric chloride and potassium iodide.	Copper deposits readily.	Slow.	Solutions decolorise.
Copper sulphate.	Very slow deposition of copper.	None.	—
Fehling's solution.	" "	Slow.	—
Cupric nitrate.	Scarcely any action.	—	—
Ammoniacal copper solution.	No action.	—	—
Ferric chloride.	Dark powder deposits.	Slow.	—
Ferrous sulphate.	No action.	—	—
Zinc chloride.	No action.	—	—
Zinc sulphate.	"	—	—
Alkaline solution of zincate.	Grey crystalline powder.	Slow.	—

Active Aluminium.

Aluminium when active, that is, when dipping into a solution of hydrochloric acid or alkali hydroxide, decomposes water vigorously and cannot be used for precise *E.M.F.* measurements.

Neumann (*loc. cit.*) therefore used amalgamated aluminium, which causes less rapid evolution of hydrogen. He obtained as the mean value of rather variable potentials: in *N*-aluminium sulphate solution -1.317 volts, in *N*-aluminium chloride solution -1.292 volts, in *N*-aluminium nitrate solution -1.052 volts, referred to the normal hydrogen electrode as zero.

Even such an electrode is far from being a reversible one, since the hydrogen ions discharging on the electrode make the potential more positive, just as silver ions do in silver concentration cells. If the evolution of hydrogen could be prevented, that is, if the potential of hydrogen could be lowered below that of aluminium, a reversible aluminium electrode would be obtained.

The potential of amalgamated aluminium wires in $0.0213N$ -aluminium chloride solution saturated with hydrogen under atmospheric pressure was, indeed, found to be less variable and more negative, namely, -1.330 ± 0.003 volts, but slow evolution of hydrogen could not be prevented.

The high overvoltage of hydrogen on a mercury surface makes it possible for a dilute amalgam of a very negative metal to behave as a reversible electrode, because the evolution of hydrogen is almost entirely prevented.

Lewis (*J. Amer. Chem. Soc.*, 1910, **32**, 1458; 1912, **34**, 119; 1913, **35**, 340; 1915, **37**, 1893) has been able to determine the electrolytic potentials of alkali metals using dilute amalgams, and the same method has been adopted here for aluminium.

Preparation of Aluminium Amalgam.—About 0.4 gram of aluminium (99.6 per cent.) was dissolved in 200 grams of pure dry mercury by boiling for two to three hours in an atmosphere of dry carbon dioxide. On cooling, some solid amalgam separated out on the surface, showing that this very dilute (about 0.1 per cent.) amalgam is saturated. This amalgam is extremely easily decomposed in moist air, instantly losing its lustre and becoming covered by hydroxide, this being no doubt due to the great affinity of aluminium for oxygen and its small affinity for mercury.

Whether this saturated amalgam shows any difference of potential from pure active aluminium or not could not be ascertained, since aluminium was found to be passive in dry acetone, ether, or piperidine. However, since the liquid amalgam is in contact with solid amalgam, their solution tensions must be identical, and as

the aluminium seems to be very loosely bound to mercury, the heat of oxidation of the solid amalgam has been found to be the same as the heat of oxidation of aluminium (Baille and Féry, *Ann. Chim. Phys.*, 1889, [vi], 17, 246). The electrolytic potential of the liquid amalgam must be very near to that of ideal active aluminium.

Measurement of E.M.F.—The glass apparatus in which the amalgam had been prepared was inverted, and the amalgam allowed to pass through a side tap, by which the flow could be regulated, into a sealed-on capillary tube (of 1 mm. bore) with a platinum contact. The lower end of the capillary tube was bent up and opened out, so as to provide a larger surface of amalgam. The electrode dipped into a solution of aluminium chloride, which was stirred by means of a stream of hydrogen bubbles. The space above the solution was thus kept filled with hydrogen under atmospheric pressure.

The second electrode was a hydrogen electrode consisting of platinum coated on glass, as used by Loomis and Acree (*Amer. Chem. J.*, 1911, 46, 585, 621, 638); there was also a calomel electrode attached to the vessel, filled with the same aluminium chloride solution, to check the hydrogen electrode from time to time. The whole apparatus was kept in a thermostat at 25.0°.

At the beginning of each experiment, hydrogen was passed through the cell until the potential difference between the calomel and hydrogen electrode became constant. Then the tap on the capillary tube was opened and the amalgam allowed to drop out slowly. It was found better to allow the amalgam to flow slowly, as on fresh surfaces, after a few seconds, bubbles of hydrogen appeared. Since, however, during readings, the potential increased by several millivolts, this being no doubt due to electrical adsorption of ions on drops of mercury, the solution round the electrode was stirred by bubbling hydrogen through it, and simultaneously the aluminium chloride solution, through which hydrogen was first passed, was allowed to flow into the space round the electrode.

A second series of measurements was made with new amalgams and capillary tubes, and the results obtained did not differ by more than 10 millivolts from the first series, even in the most dilute solutions, whilst in the stronger solutions the agreement was within 3 millivolts.

In this way, the following readings were obtained (using accumulator, Weston cell, Lippmann electrometer, and potentiometer giving readings to 0.1 millivolt):

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Concentration of aluminium chlorides in gram-equivalents per litre.	Mean <i>E.M.F.</i> of the cell: $+H_2 \left \begin{array}{c} AlCl_3 \\ \text{solution} \end{array} \right \begin{array}{c} Al- \\ \text{amalgam.} \end{array}$	π_{Al} referred to the normal hydrogen electrode.
(2.88	1.128 volt	-1.284 volt)
0.1845	1.164	-1.370
0.0875	1.160	-1.382
0.0337	1.157	-1.383
0.0213	1.145	-1.381
0.0107	1.161	-1.397
(0.00675	1.135	-1.381)
(0.00213	1.136	-1.377)

The determinations of single hydrogen electrode potentials are described in the preceding paper (p. 15), from which the potentials of aluminium amalgam electrodes, π_{Al} (third column), could be calculated.

The solutions were prepared from aluminium chloride purified by precipitation with hydrogen chloride, and to each solution excess of freshly precipitated aluminium hydroxide was added. In such solutions, the solubility product $[Al^{+++}].[OH']^3$ should be constant and equal to $k.[Al(OH)_3]$. Then the electrolytic potential of aluminium becomes

$$E.P. = -\frac{R.T}{3F} \log_e \frac{C_{Al}}{[Al^{+++}]} = -\frac{R.T}{3F} \log_e \frac{C_{Al} [OH']^3}{k} =$$

$$-\frac{R.T}{F} \log_e \frac{C_{Al}^{\frac{1}{3}} \cdot K}{[H']} = -\frac{R.T}{F} \log_e K \cdot [OH']$$

where K is a constant.

Such an electrode, therefore, behaves as a hydrogen electrode or an oxygen electrode of the type $Hg|HgO$, and consequently its potential, π_{Al} , should always differ from the platinised electrode by a constant.

The difference between the two electrodes (column 2) is very nearly constant, except in the case of the first solution, which was very viscous and opaque. In the two most dilute solutions the *E.M.F.*'s were rather variable, sometimes approaching 1.16 volts. The value of π_{Al} on the whole falls with the increase of acidity and concentration of aluminium chloride.

In order to determine how the potential of the aluminium electrode is influenced by different solutions, a simpler form of apparatus was used, having two capillary amalgam electrodes dipping into solutions saturated with hydrogen and covered by a layer of liquid paraffin. In this case, the amalgam was not allowed to drop continuously, but the surface was renewed every few minutes.

The values obtained in this way (at 25°) are given in table I. Single potentials are referred to the normal hydrogen electrode.

TABLE I.

Solution used in the Al-electrode.	Second electrode, Calomel of the same solution.	Observed <i>E.M.F.</i> in volts.	Potential of Al-electrode, π_{Al} .	π_H potential of H_2 hydrogen electrode, dipping in the solution used.	<i>P.D.</i> between the Al and H_2 electrode, when both in the same solution $= \pi_H - \pi_{Al}$.	Concentration of hydriions of the solution used.
<i>N/10</i> -HCl	<i>N/10</i> -KCl calomel.	1.5790	-1.209	-0.057	1.152	10^{-1}
2.90 <i>N</i> -AlCl ₃	<i>N</i> -KCl calomel.	1.54—1.55	1.26—1.27	-0.110	1.15—1.16	8.10^{-2}
0.368 "	Calomel of the same solution.	1.474	1.374	0.181	1.193	10^{-2}
0.0675 "	"	1.499	1.359	0.202	1.157	4.10^{-4}
0.0409 "	"	1.702	1.342	0.208	1.134	3.10^{-4}
0.0184 "	"	1.724	1.343	0.214	1.129	2.10^{-4}
0.0046 "	"	1.755	1.349	0.230	1.119	$1.4.10^{-4}$
0.00306 "	"	1.770	1.345	0.233	1.112	$1.1.10^{-4}$
0.0028 "	<i>N</i> -KCl calomel.	1.630	1.347	0.237	1.110	10^{-4}
0.30 <i>N</i> -Al ₂ (SO ₄) ₃	"	1.700	1.417	—	—	—
0.030 "	"	1.742	1.459	—	—	—
<i>N/10</i> -KCl	"	1.785	1.502	0.415	1.087	10^{-7}
<i>N</i> -KCl	"	1.750	1.497	0.415	1.052	10^{-7}
<i>N/100</i> -KOH + Al(OH) ₃	Hg + HgO of the same solution.	1.910	1.622	0.628	0.994	10^{-11}
<i>N/10</i> . " "	"	1.774	1.576	0.718	0.858	10^{-13}
<i>N/10</i> -KOH	"	1.752	1.613	0.777	0.836	10^{-12}
<i>N</i> -KOH saturated with Al(OH) ₃	"	1.713	1.596	0.799	0.797	10^{-12}

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Some determinations of single electrode potentials, π_{Al} and π_H , are calculated from the results described in the preceding paper, the electrode potentials in potassium hydroxide solutions were obtained by elimination of the diffusion potential with concentrated potassium chloride solutions.

With fresh surfaces, the *E.M.F.* rose a few millivolts to a maximum, and after three minutes began to fall slowly. If the solution round the electrode was stirred or the electrode shaken, the *E.M.F.* fell about 20 millivolts, but reverted to the original value on keeping. Oxidising agents, such as dilute solutions of ferric chloride or hydrogen peroxide, or even a current of air, caused a considerable decrease of negative potential, amounting to several decivolts; reducing agents had no influence.

The more acidic the solution, the more stable was the *E.M.F.* and fewer bubbles of hydrogen appeared on the surface of the amalgam. In *N*/10-hydrochloric acid no bubbles were formed, and the *E.M.F.* was constant for ten minutes at 1.5788 volts, whereas in alkaline solutions there was a visible evolution of minute bubbles.

Discussion of Results.

From the most trustworthy measurements of π_{Al} in

0.1845 <i>N</i> -AlCl ₃	= -1.370 volts,	where [Al'''] = 0.0130*
0.0675 ,,	= -1.382 ,,	,, = 0.0080
0.0337 ,,	= -1.383 ,,	,, = 0.0044

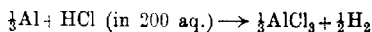
the theoretical value for the electrolytic potential of aluminium in a normal solution of aluminium ions *E.P.* has been calculated by the formula

$$E.P. = \pi_{Al} - \frac{RT}{3F} \log_e [Al'''] = \pi_{Al} - \frac{0.0591}{3} \log_{10} [Al'''].$$

The values -1.333, -1.341, -1.336 calculated in this way give *E.P.* = -1.337 volts as the most probable value.

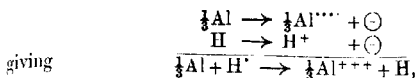
The approximate value of the electrode potential can be obtained from the heat of the electro-chemical reaction if we neglect the term $T \cdot \frac{d\pi}{dT}$ in the equation $\pi = Q + T \cdot \frac{d\pi}{dT}$ and assume that the heat equivalent, *Q*, of the reaction is equal to the total change of energy.

The heat of the reaction

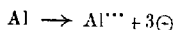


See Part I.

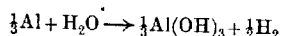
is 41·033 calories (Thomsen). It can be regarded as the difference of heats of ionisation of the processes:



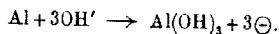
from which the calculated potential of the process



is 1·76 volts, whereas the potential corresponding with 31·000 calories of the reaction

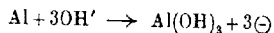


leads to 1·34 volts. This would apply to the electrochemical process



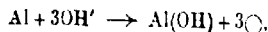
The coincidence of the latter value with the observed one was pointed out by Kistiakovsky (*Zeitsch. physikal. Chem.*, 1910, **70**, 260), who suggested similar electrode reactions for magnesium, iron, and chromium.

The reason why only the process



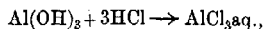
is the source of electrical energy must be sought in the extremely small solubility product of aluminium hydroxide ($=10^{-33}$; see Part I) effecting considerable hydrolysis. Owing to this, the layer of solution close to the surface of the amalgam is saturated with aluminium hydroxide, so that the potential is determined by hydroxyl ion concentration directly, by aluminium ion concentration only through the solubility product equilibrium. This is evident from table I, where with decreasing acidity π_{Al} increases. Owing, however, to increasing oxidation of the amalgam in less acidic solutions, the values are shifted towards more positive potentials, so that in these solutions the potential density from the hydrogen electrode (column 4, table I) decreases instead of being constant.

The reason why even in acidic solutions (like 0·1N-hydrochloric acid) the ordinary ionisation potential of $\text{Al} \rightarrow \text{Al}^{+++} + 3\ominus$ is not attained, but the value remains, roughly, that of



must be sought in the extremely slight dissociation of aluminium hydroxide, which does not react sufficiently quickly with the acid to form aluminium ions, and remains far behind the reaction

determining the *electrode potential*. Moreover, the second reaction might be a molecular one, not ionic, thus:



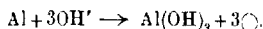
and need not take place at the electrode.

Summary.

(1) Various potentials of passive aluminium have been measured, and the influence of the anion on potential, dissolution, and deposition of metals is discussed.

(2) The potential of active aluminium in the form of saturated liquid amalgam has been measured in different solutions.

(3) The theoretical value of *E.P.* = -1.337 volts at 25°, the normal hydrogen electrode being taken as zero. The corresponding electrochemical reaction being



In conclusion, I desire to express my thanks to Prof. F. G. Donnan, at whose suggestion this work was undertaken, for his kind interest and advice. I also wish to express my indebtedness to Dr. R. E. Slade for his constant help throughout this investigation.

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V.—The Propagation of Flame in Mixtures of Methane and Air. Part I. Horizontal Propagation.

By WALTER MASON and RICHARD VERNON WHEELER.

IN previous communications to this Society a study of the initial "uniform movement" of flame in gaseous mixtures has been presented (T., 1917, 111, 267, 1044; 1919, 115, 578). The majority of the experiments of which an account has been given have been with methane as the combustible gas. The general conclusions drawn as to the character and rationale of the uniform movement are, however, applicable to all inflammable mixtures.

The uniform movement is one phase in the propagation of flame, and is of comparatively short duration. The speeds attained by the

flames during its regime are comparatively slow; very slow compared with that of the detonation-wave, but slow also compared with the speeds during other phases in the propagation of flame in mixtures wherein the detonation-wave normally does not develop.

The value of determinations of the speeds of flames during the uniform movement lies in the measure thereby afforded of the general behaviour of a given inflammable mixture or range of mixtures immediately after ignition, the measurements, when made under standard conditions, being physical constants. Knowledge is, however, often necessary of the maximum speed attainable at any time during the course of the propagation of flame in mixtures of a given combustible gas with air or oxygen. Such knowledge is of prime importance, for example, in respect of mixtures of methane and air, in connexion with the safe working of coal mines.

In the present paper a description is given of the phases, other than the uniform movement, during the horizontal propagation of flame in mixtures of methane and air.

The several series of experiments were carried out in tubes of different dimensions and materials. It is important when comparing one series of experiments with another that due regard should be paid to the details given respecting the tubes employed. In the majority of the experiments measurements of speeds were made by the "screen-wire" method, of which full details have been given in earlier papers (T., 1914, 105, 2610; 1917, 111, 1053). Supplementary information was obtained by photographic analysis of the flames. In order to obtain the photographs the flames were caused to travel along a tube of brass, 5 cm. in diameter, furnished with a window of quartz which was focussed on a rapidly revolving film by means of a quartz lens. The use of quartz enabled the light falling on the film to be sufficiently actinic to record the movements of the flames with considerable detail.

(1) Ignition at the Open End of a Tube Closed at the Other End.

The initial phase of propagation of flame when the mixture is contained in a horizontal tube closed at one end and open at the other, and ignition is at the open end, constitutes the "uniform movement."

The linear duration of the uniform movement is controlled by the speed of the flame (and thus by the composition of the inflammable mixture); by the length, diameter, and uniformity of bore of the tube; in short, by such factors as influence the establishment of resonance in the column of gases in the tube. Eventually, as a direct outcome of the establishment of resonance, the flame-front

acquires a periodic undulatory motion (see T., 1919, 115, 584) leading sooner or later to violent vibrations which vary considerably in amplitude but remain periodic.

This phase in the propagation of flame was discovered by Schloesing and de Mondésir, and was termed "le mouvement vibratoire" by Mallard and Le Chatelier (*Ann. des Mines*, 1883, [viii], 4, 331). Although accurate record can be obtained of the development of the "vibratory movement" under chosen conditions, the measurements—of the mean speed of the flame, for example—are not of much theoretical significance or practical value, for the speed of the flame during any one vibration, and the amplitude of the vibrations, is very susceptible of changes, designed or inadvertent, in the experimental conditions.

So far as mixtures of methane and air are concerned, it is perhaps sufficient to record a few of the data obtained as indicative of the general character of this phase in the propagation of flame for comparison with the uniform movement which precedes it. Thus, with mixtures containing between 10 and 10.5 per cent. of methane, and with a tube of brass 240 cm. long and 5 cm. in diameter, the significant measurements, obtained by photographic means, are as follow:

Speed of flame during uniform movement	...	90 cm. per second.
Linear duration of uniform movement	...	80 cm.

Faint undulations of the flame-front appear after the flame has travelled 32 cm. The mean speed of the flame is not affected by these undulations; their amplitude is small, and their period is that of the resonating column of gases in the tube. The amplitude of the undulations increases gradually from 1.7 cm. over the distance 32—50 cm. to 1.9 cm. over the distance 50—60 cm. and 2.2 cm. over the distance 60—80 cm. It then begins to increase rapidly, becoming 3.6 over the distance 80—90 cm. During this period of rapid increase in amplitude of the undulations the mean speed of the flame falls to 64 cm. per second. Eventually, the "vibratory movement," which owes its origin to an undulation of abnormal amplitude, is established.

During the vibratory movement the oscillations of the flame are of wide amplitude—25 cm. or more—and the mean speed of translation of flame is considerably enhanced. It will be seen on examination of Plate 1, Fig. 1, that the change of speed from that of the uniform movement (90 cm. per sec.) to that of the vibratory movement (278 cm. per sec.) is fairly abrupt, and that the latter speed is maintained at a constant mean value over a considerable distance. Finally, as the flame approaches the closed end of the tube,

its mean speed decreases, although it still continues to vibrate to the end.

In the table that follows, data are given respecting successive portions of the vibratory movement, each portion being specified by the distance along the tube over which the flame travelled.

Vibratory Movement of Flame.

(Tube of brass 240 cm. long and 5 cm. in diameter. Methane 10—10·5 per cent. in air.)

Distance along tube.	Mean speed of flame. Cm. per sec.	Maximum speed during forward motion of flame. Cm. per sec.	Amplitude of motion of flame. Cm.	Frequency of vibrations. Mean values.
0—80 cm.	—	Uniform movement	—	—
80—90	64	292	3·6	47·7
90—107	—	Gradual change	—	—
107—170	278	2,430	26·0	70·0
170—200	—	Gradual change	—	—
200—220	62	416	1·4	45·0
220—240	38	—	—	—

It may be noted that, as indicated by the frequency of the vibrations, the resonating column of gases is that lying between the closed end of the tube and the flame-front at any given moment. Thus the calculated mean value for the frequency of vibration of a column of gases in an unflanged tube of brass 5 cm. in diameter is 48 if the tube is 130—140 cm. long and 74·5 if it is 50—93 cm. long.

These measurements bear reference only to the particular conditions of experiment specified, but they could be reproduced with an exactness which must be considered remarkable when the complicated character of the phenomena is borne in mind. In this respect better fortune has attended the experiments than that which befel Mallard and Le Chatelier, who have stated: "*En répétant plusieurs fois la même expérience dans des conditions identiques à elles-mêmes, le mouvement vibratoire ne se reproduit jamais deux fois de la même façon*" (*loc. cit.*, p. 333). No doubt the rapid speed of flame in the mixture ($\text{CS}_2 + 6\text{NO}$) employed by Mallard and Le Chatelier for their experiments would tend to emphasise irregularities in the results.

It has already been stated that the vibratory movement is the direct result of the resonance of the column of gases in the tube. It was shown, in connexion with experiments on the propagation of flame in mixtures of acetylene and air, that resonance, by whatever means induced, can be made manifest by the undulatory motion of flame as it travels along tubes, the periods of the undulations agreeing closely with the periods calculated for organ-pipes of the dimen-

sions of the tubes employed. As the resonance becomes stronger, the amplitude of the undulations of the flame front perforce increases, since the flame acquires its motion from the vibrating column of gases. There is thus produced an agitation of the gaseous mixture which eventually becomes of sufficient importance to affect appreciably the speed of a flame travelling through it. (In this connexion, see T., 1919, 115, 81.)

The vibratory movement is, indeed, an excellent example of the effect of agitation or turbulence in accelerating the translation of flame through a gaseous mixture. The effect is a mechanical one. During each forward impulse the flame is drawn rapidly through previously unburnt mixture by reason of the motion acquired by the resonating column of gases. In a certain degree, also, the forward motion of the flame is assisted by the expansion in volume of the burning gases, especially when the flame is at some distance from the open end of the tube, so that escape of the expanded gases there is retarded. The latter effect is more pronounced when the mixture is ignited at the closed end of a tube open at the other end, conditions which will be considered in the succeeding section of this paper.

(II) *Ignition at the Closed End of a Tube Open at the Other End.*

The two phases in the propagation of flame, the "uniform movement" and the "vibratory movement," are characteristic of what occurs with mixtures of a combustible gas and air when ignition is at the open end of a tube closed at the other end. Under such conditions, with some combustible gases (for example, hydrogen) when mixed with air, and with all when mixed with pure oxygen, the vibratory movement is succeeded by the detonation-wave, provided that the combustible gas and oxygen are in suitable proportions.

With no mixture of methane and air (at atmospheric temperature and pressure) is the detonation-wave thus developed, but the vibratory movement continues until the flame is extinguished, either on reaching the closed end of the tube or, occasionally, during an abnormally extensive backward movement, before the end is reached.

When ignition of a mixture of methane and air is at the closed end of a tube open at the other, no uniform movement takes place, but the speed of the flame increases rapidly as it travels towards the open end.

For comparison with the uniform and vibratory movements, experiments were made with a series of mixtures in a horizontal tube of glass 5 cm. in diameter and 500 cm. long. Fine screen-

wires of copper were stretched across the tube at half-metre distances, and the times taken for the flames to travel between these screen-wires measured by the method described in previous communications. The mixtures were ignited at a spark-gap 3 cm. from the closed end.

The speed of the flame in some of the mixtures reached 29 m. per second over the last half-metre length of the tube, and, so far as could be judged, was nearly uniformly accelerated from the beginning. It seemed possible, therefore, that with a tube of greater length and larger diameter a permanent maximum velocity of flame, such as is characteristic of the detonation-wave, might eventually be attained.

A steel tube 30.5 cm. in diameter and 90 m. long was used to test this supposition. It was found that flame did not continue to propagate in any mixture beyond a distance of 15 m. from the closed end, at which ignition was effected. Violent vibrations were developed after the flame had travelled 10 m., in the course of which the flame was extinguished. The same result was obtained when the mixtures were ignited a few cm. (ten to twenty) from, instead of at, the closed end, a condition which would have the effect of imparting an impetus to the flame at the beginning, thereby hastening the development of the detonation-wave (compare Dixon, *Phil. Trans.*, 1903, A., 200, 345).

The extinction of the flame after travelling such a short distance in a long tube under the conditions of these experiments is no doubt caused by the products of combustion, when cooling, tending to produce a partial vacuum behind the flame (the end of the tube from which the flame started being sealed), which is therefore dragged back over part of the path it has already travelled. This may occur several times, the flame alternately leaping forward and being drawn back, but eventually a sufficient proportion of the burnt mingles with the unburnt gases to prevent further propagation of flame.

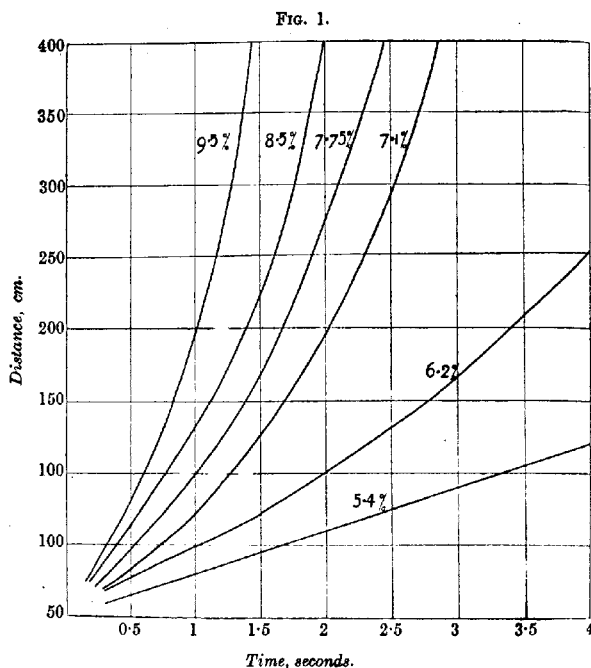
(III) Ignition at One End of a Tube open at Both Ends.

If the reason assigned for the extinction of the flame when travelling from the closed to the open end of a long tube is correct—a reason intended to apply only to such comparatively slowly-moving flames as are obtained with mixtures of methane and air*—extinc-

* With mixtures of coal-gas and air, for example, in which the flames are initially more rapid than with methane and air, the vibratory movement continues (in a steel tube 30.5 cm. in diameter) until the detonation-wave is developed. The speed of the wave, in a mixture containing 17 per cent. of coal-gas, is 1750 m. per second.

tion should not occur when both ends are open (so that the cooling of the products of combustion cannot create a partial vacuum behind the flame), and the speed at which the flame travels should be rapid.

Several series of experiments were made to test this point, it being important to determine the conditions under which the most rapidly moving flames are obtained in mixtures of methane and air, and the order of magnitude of the speeds.



The first series of experiments was in a tube of glass 5 cm. in diameter and 500 cm. long, for comparison with the series, carried out in the same tube, in which ignition was at a closed end. The results are shown graphically in Fig. 1, in which distance along the tube is plotted against time, zero time being the moment of fusion of the first screen-wire, which was 10 cm. from the point of ignition.

With all but the lower-limit mixture (5.40 per cent. methane), in which the speed of flame is uniform, there is a gradual and, so

far as the records can indicate, regular acceleration of speed as the flame travels from end to end of the tube. In no instance did extinction of the flame occur, although in most of the experiments slight vibrations were noticed at different stages in the development of the propagation, the incidence of these vibrations being earlier the more rapid was the flame. There was, also, with the mixtures richer in methane, a noticeable check in the progress of the flame as it approached a particular point, succeeded by a spurt forward after that point had been passed. This effect seemed traceable to a slight ridge around one of the small holes with which the tube had been pierced (by means of a blow-pipe flame) to receive the screen-wires used to record the time of passage of the flame. This ridge projected less than 1.5 mm. within the tube; the fact that it could markedly affect the progress of a flame in a tube 50 mm. in diameter is a striking example of the sensitiveness of flames to turbulence in the mixture, even such slight turbulence as the small projecting ridge would cause. This subject will be dealt with in a subsequent communication.

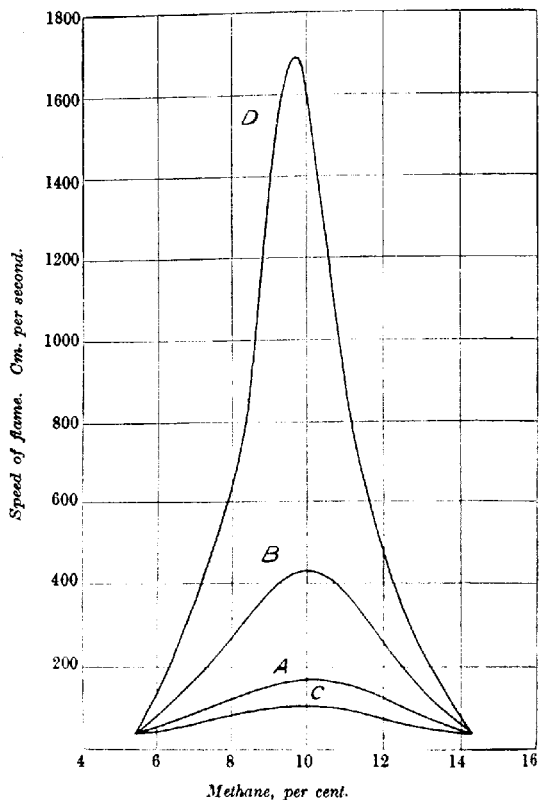
Another series of experiments covered the whole range of inflammable mixtures of methane and air, and was made in a glass tube 9 cm. in diameter and 620 cm. long. This series is of value for comparison of the mean speeds of the flame over measured distances with the speeds of the uniform movement in a tube of the same diameter. Such a comparison is made diagrammatically in Fig. 2, which records speed-percentage curves (*A*) for the distance (measured from the point of ignition) 50—100 cm., and (*B*) for the distance 407—467 cm. in the tube open at both ends, the speeds being the mean speeds of the flames over those distances; and (*C*) for the uniform movement. In addition, a curve (*D*) is given showing the mean speed of flame over the distance 20—120 cm. in a tube 5 cm. in diameter closed at one end and open at the other, ignition being at the closed end.

The mean speed over the distance 407—467 is seen to be greatest in the mixture containing 10 per cent. of methane, and to be about four times the speed of the uniform movement in that mixture in a tube of the same diameter. The speed of the flame in all mixtures (except the limit mixtures) was found, as with the tube of 5 cm. in diameter, to increase continuously over the whole distance travelled, and, as when ignition was at the closed end of a similar tube, it seemed possible that the detonation-wave might be developed if the flame could travel far enough. If not, it was necessary to know what change in the character of the propagation would interpose to prevent it.

The steel tube, 30.5 cm. in diameter, was brought into requisition

to test this. The length of the tube in the first instance was 15.25 m., and records were obtained of the times taken for the flame to travel measured distances from the point of ignition in different mixtures. As usual, the fastest speed of flame was obtained with mixtures containing between 9.5 and 10.5 per cent.

FIG. 2.



of methane, but no speed approaching that of the detonation-wave was recorded, the maximum being 917 cm. per second, attained after travelling 14 m. in a mixture containing 10.25 per cent. of methane.

It appeared from the records that the flame, which could not be

directly observed, had acquired a vibratory character after travelling half the length of the tube. No indication of this was given by the sound of the flames as they travelled, and the vibrations were presumably of small amplitude. Vibratory propagation in the steel tube, such as was obtained when one end of the tube was closed, had hitherto been accompanied by a staccato note, but the flames now produced seemed, to the ear, to travel unhaltingly from one end of the tube to the other, issuing into the air with a sharp report.

The length of the tube was therefore increased to 90 m. in the expectation that, if the flame had indeed become vibratory in character after travelling 6 or 7 m., a greatly increased distance of travel would produce readily recognisable vibrations of large amplitude. Such was, in fact, the result; the propagation ultimately became strongly vibratory, but the early stages of the propagation were profoundly modified by the increased length given to the tube. Instead of increasing rapidly in speed from the beginning, as when the tube was 15.25 m. in length, the flames now travelled from the point of ignition at a constant and comparatively slow speed over a distance of between 12 and 15 m. (dependent on the composition of the mixture) and then began to vibrate. The vibrations acquired their greatest amplitude about half-way along the tube and continued throughout the remaining distance.

In mixtures containing between 9.5 and 10.5 per cent. of methane the speed of the flame over the first 12—15 m. averaged 200 cm. per second. Thus, the records obtained over this range of mixtures were:

Methane. per cent.	Initial speed of flame. Cm. per second.
9.60	198
9.70	188
9.75	203
10.10	213

This speed is a little faster than that of the uniform movement in similar mixtures in the same tube (170 cm. per second). The important point is, however, that the speed should remain constant over so great a distance. Although open at both ends, a long tube is thus found to impress upon a flame started at one end conditions similar to those obtaining with a shorter tube closed at the distant end. The resistance to the expansive force of the burning gases afforded by the long column of unburnt mixture in advance of the flame corresponds (nearly) in effect with the resistance of a closed end; so close is the correspondence that the flame is caused to proceed at the outset with a "uniform movement," but little faster

than the uniform movement as ordinarily developed in mixtures of the same methane-content in a tube of the same diameter.

Photographic Analysis of the Flames.

In Plate 1 are shown time-distance curves, obtained photographically, for the propagation of flame in a 10 per cent. mixture of methane and air in a tube of brass 5 cm. in diameter and 240 cm. long.

The flames travelled horizontally from right to left, and the photographic film can be regarded as moving vertically upwards, its speed of travel being 30 cm. per second. The full length of the tube, 240 cm., is shown in the photographs, each of which is composite, being obtained by joining together photographs of successive sections of the tube 30 cm. in length.

For Fig. 1 the tube was closed at the left-hand end, and ignition was at the right-hand, open, end; for Fig. 2 the tube was open at both ends, and ignition was at the right-hand end; and for Fig. 3 the right-hand end of the tube was closed, and ignition was effected there, the left-hand end being open.

The relative speeds at which the flame traversed the full length of the tube are readily deduced from these photographs, which also illustrate the general behaviour of the flames under the different conditions of ignition of the mixtures, and require no description. It should be noted, however, that Fig. 3 discloses the presence of rapid vibrations during the progress of the flame which, as stated earlier in this paper, was judged by visual observation to travel unchecked through the tube at a speed which, according to determinations by the screen-wire method, seemed to be nearly uniformly accelerated.

In Plates 2 and 3 details of the flames as they passed through a section of the tube 30 cm. in length are shown, the section chosen being that indicated in Plate 1 by the vertical white lines. To obtain these photographs the speed of the film was increased to 90 cm. per second. Calculations made from them are as follow:

PLATE 2.

Tube closed at one end; ignition at open end.

Mean speed of flame	245 cm. per sec.
Maximum speed during forward movement of vibration	1,990 cm. per sec.
Average frequency of vibrations	76

The calculated frequency for the fundamental tone of the tube during the longitudinal vibration of air within it is 68 if the length

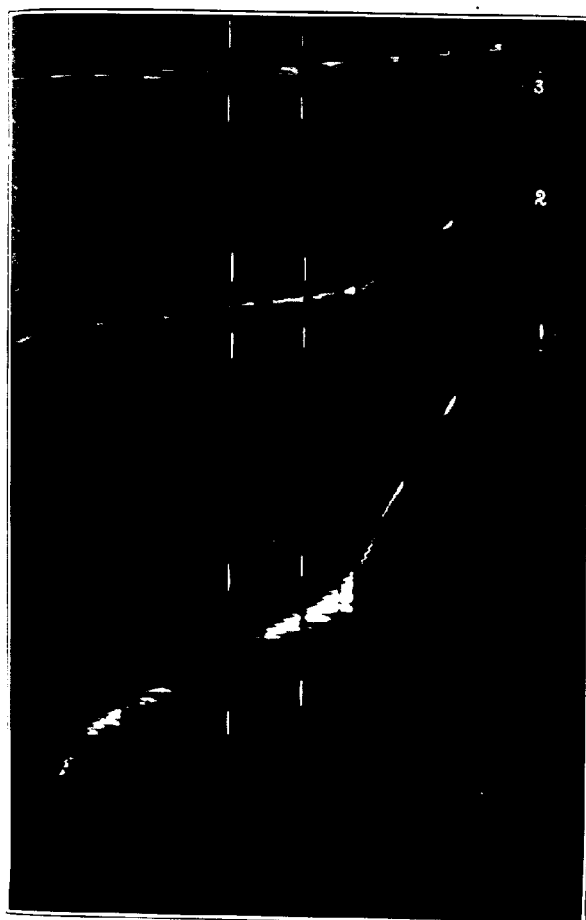


FIGURE 1. $\log R$ versus $\log C$.

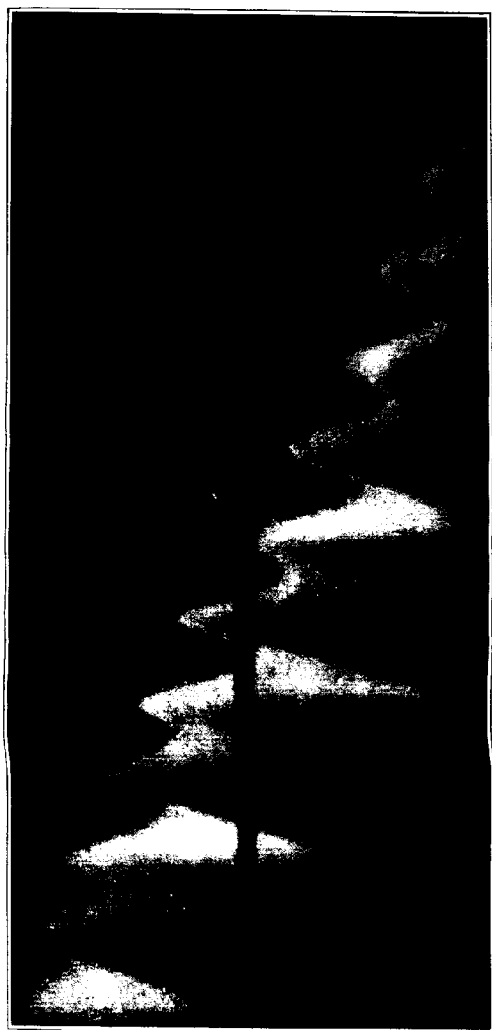


FIG. 2

FIG. 1.



FIG. 2.

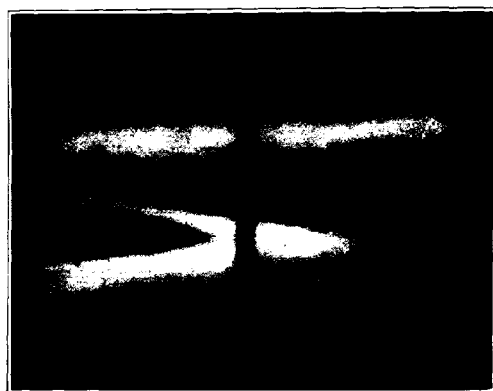


PLATE 3.

of the vibrating column be assumed to be 125 cm. and 88 if 95 cm. These are the distances of the flame-front from the closed end of the tube at the beginning and end of the photograph respectively. The mean value is 78.

PLATE 3, FIG. 1.

Tube open at both ends; ignition at one end.

Mean speed of flame	480 cm. per sec.
Maximum speed during forward movement of vibration	3,730 cm. per sec.

PLATE 3, FIG. 2.

Tube closed at one end; ignition at closed end.

Mean speed of flame	1,050 cm. per sec.
Maximum speed during forward movement of vibration	5,760 cm. per sec.
Amplitude of vibrations	30 cm.

Of the three conditions under which the ignition of mixtures of methane and air has been effected in these experiments, that which would lead to the most disastrous results in industry is the third—ignition at one end of a tube or gallery open at both ends. For although the initial speed of the flame is not then so great as when ignition is at a closed end, continued propagation is assured, and there may be developed momentarily during the vibratory motion velocities and pressures as great as any produced throughout the life of a flame started at a closed end.

The fastest speed of flame recorded in any experiment was about 60 m. per second, and was of short duration. This is not of the same order of magnitude as the speed of the detonation-wave in gaseous mixtures. It would not be wise to conclude, however, that the detonation-wave cannot, in any circumstances, be developed in mixtures of methane and air at normal temperature and pressure. On the contrary, in several experiments in the steel tube, 90 m. long and open at both ends, in which restrictions were introduced at two points (consisting of steel rings which reduced the diameter of the tube to 28.6 cm. at those points), the development of the detonation-wave seemed imminent. Further description of these experiments, which are being continued, is reserved until the subject of the effects of turbulence on the propagation of flame in gaseous mixtures is discussed.

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[Received, December 4th, 1919.]

VI.—*The Propagation of Flame in Complex Gaseous Mixtures. Part IV. The Uniform Movement of Flame in Mixtures of Methane, Oxygen, and Nitrogen. "Maximum-speed Mixtures" of Methane and Hydrogen in Air.*

By WILLIAM PAYMAN.

It is customary to describe the inflammation of a gas mixture containing hydrogen and oxygen, for example, as the "burning of hydrogen in oxygen." This phrase is purely a relative one, it being, of course, equally correct to regard the combustion as the burning of oxygen in hydrogen. Thus the upper limit of inflammability of hydrogen in oxygen is the lower limit of inflammability of oxygen in hydrogen.

Mixtures of a combustible gas with air can be considered in a similar way. If, however, we state that the combustible gas, hydrogen, for example, is burning in air, the alternative expression would be that the oxygen is burning in a mixture of nitrogen and hydrogen. A comparison can, in fact, be made over a range of inflammable mixtures, between hydrogen and air on the one hand, and, on the other, mixtures of oxygen with a mixture (or "atmosphere") containing nitrogen and hydrogen in constant proportions.

For all practical purposes, atmospheric air may be regarded as a mixture of oxygen and nitrogen in constant proportions. To investigate thoroughly the mode of combustion of complex inflammable gas mixtures, it is evidently desirable to examine their behaviour with "atmospheres" other than air, the simplest problem being no doubt the combustion of a pure, inflammable gas, such as methane, in pure oxygen.

The uniform movement during the propagation of flame in mixtures of methane with different atmospheres containing less oxygen than air has been examined by Mason and Wheeler (T., 1917, 111, 1044). The present research deals with mixtures containing more oxygen than air, and with mixtures with pure oxygen. The detonation-wave in such mixtures has been studied by Dixon (*Phil. Trans.*, 1893, 184, 97). The speed of propagation of flame by detonation is of a different order from that during the initial, uniform movement of flame, which is supposed to be mainly effected by the conduction of heat from the burning to the adjacent unburnt

layer of gas mixture. The speed of the detonation-wave is, however, uniform. The two modes of propagation of flame, "uniform movement" and "detonation-wave," may be compared with respect to mixtures of hydrogen and air. The speed of the detonation-wave in the mixture of air with hydrogen containing the correct proportions for complete combustion is 1930 metres per second in a tube 9 mm. in diameter (value extrapolated from those determined by Dixon, *loc. cit.*), whilst the speed of the uniform movement of flame in the same mixture (in a horizontal glass tube 2.5 cm. in diameter) is 4.8 metres per second (Haward and Otagawa, T., 1916, 109, 83).

Maximum-speed Mixtures.—If we neglect losses of heat to the walls of the containing vessel, the speed of propagation of flame during the uniform movement can be regarded as depending mainly on two factors, namely, (1) the rate of conduction of heat from layer to layer of the mixture, which in turn depends on the difference in temperature of the burning and the unburnt gases and on their thermal conductivities, and (2) the rate of reaction of the combining gases, which for a given combustible gas will vary with the composition of the mixtures (presumably according to the usual laws of mass action) and with the temperature produced by the reaction. A third factor might be added, namely, the ignition-temperature of the mixtures, but this is perhaps dependent on the other factors.

The mixture of hydrogen and air for complete combustion, that is to say, the mixture having the greatest heat of combustion, contains 29.6 per cent. of hydrogen, but the mixture in which the speed of the uniform movement of flame is greatest contains about 38 per cent., or nearly 10 per cent. in excess. This fact is usually explained by reference to the high thermal conductivity of hydrogen, which is 31.9×10^{-5} , as compared with 5.22×10^{-5} for air. A similar displacement of the maximum speed mixtures is, however, observed with all inflammable gases when mixed with air, including (as was shown in Part III of this series of papers) gases, such as carbon monoxide, the thermal conductivities of which are less than that of air.*

Consider the effect of mass action when methane burns in a given atmosphere of nitrogen and oxygen. Let this atmosphere contain a per cent. of oxygen. According to the law of mass action, the rate of reaction will be proportional to $C_{CH_4} \times C_{O_2}^2$. Let the mixture in which the rate has its maximum value contain x per cent. of methane.

* The value for the thermal conductivity of carbon monoxide is 4.99×10^{-5} .

Then

$$C_{\text{CH}_4} \times C_{\text{O}_2}^2 = (x) \times \left[(100-x) \frac{a}{100} \right]^2 \\ = x(100-x)^2 \left(\frac{a}{100} \right)^2.$$

Since a is constant, the term into which it enters will be at a maximum when $x(100-x)^2$ is at a maximum. That is to say, provided it remains constant, the composition of the atmosphere does not affect the methane content required to give the expression $C_{\text{CH}_4} \times C_{\text{O}_2}^2$ its maximum value. It can be shown that this expression reaches a maximum when x , the percentage of methane, is 33.3. Similarly, with hydrogen and any atmosphere of oxygen and nitrogen of constant proportion, the factor representing the effect of mass action is at a maximum when the mixture contains 66.7 per cent. of hydrogen.

In every instance with a given atmosphere, when this remains unaltered, the maximum effect of the mass-action factor is theoretically attainable with mixtures containing more combustible gas than is required for complete combustion (except with an atmosphere of pure oxygen, when the mixture for complete combustion is also, theoretically, that for the maximum effect of mass action).

The rate of chemical reaction increases rapidly with rise of temperature. In a series of mixtures of a combustible gas with an atmosphere of constant composition, the highest calorific effect is produced by the mixture containing combustible gas and oxygen in combining proportions. This factor will therefore act in an opposite sense to mass action and will diminish the "displacement" of the maximum speed mixture caused by the latter factor. For this reason the amount of displacement will be influenced by the cooling effect of excess of combustible gas, and the higher the specific heat of this excess gas at the temperature of reaction the less will be the displacement.*

When oxygen burns in an "atmosphere" of constant composition, composed of nitrogen and a combustible gas, the displacement of the maximum mixture should take place towards mixtures containing excess of oxygen. This can be tested experimentally. Just as the whole series of inflammable mixtures of methane and air can be obtained by starting with the mixture containing the reacting gases in combining proportions, and adding either methane or air to it, in the same way a series of mixtures of oxygen with an "atmosphere" of nitrogen and methane can be obtained, by adding excess of oxygen or excess of "atmosphere" to the

* This consideration accounts for the wider "displacement" obtained with carbon monoxide than with hydrogen when mixed with air.

mixture of methane and air in combining proportions, which may be termed the "basic mixture." This procedure has the advantage of enabling a direct comparison to be made between methane-air and oxygen-"atmosphere" mixtures, the two series having a common point.

The results of two such series of determination of the speed of the uniform movement of flame in mixtures of oxygen with (i) an atmosphere of nitrogen and methane, and (ii) one of nitrogen and hydrogen, are given in table I. The determinations were carried out in a horizontal glass tube 1.5 metres long and 2.5 cm. in diameter.

TABLE I.

Speed of Uniform Movement of Flame in Mixtures of Oxygen with Mixtures of Constant Composition ("Atmospheres") of Nitrogen and a Combustible Gas.

Methane as the combustible gas.			Hydrogen as the combustible gas.		
<i>Basic mixture</i> : 9.5 per cent. CH ₄ ; 19.0 per cent. O ₂ ; 71.5 per cent. N ₂ .			<i>Basic mixture</i> : 29.6 per cent. H ₂ ; 14.8 per cent. O ₂ ; 55.6 per cent. N ₂ .		
Methane. Per cent.	Oxygen. Per cent.	Speed. Cm. per sec.	Hydrogen. Per cent.	Oxygen. Per cent.	Speed. Cm. per sec.
6.67	43.3	35.0	16.06	53.7	171
7.51	46.2	61.9	21.76	37.3	488
8.29	39.5	84.3	25.72	25.9	660
8.75	25.6	97.3	29.60	14.8	410
9.07	22.9	91.4	30.50	12.2	234
9.18	22.0	85.4			
9.50	19.0	66.7			
9.67	17.8	37.5			

It will be seen that the displacement of the maximum-speed mixture in both series of experiments, as anticipated, is towards mixtures containing an excess of oxygen. In table II the displacements are compared with those found with the combustible gases burning in air.

TABLE II.

Displacement of Maximum-speed Mixtures.

	Methane.		Hydrogen.	
	O ₂ -N ₂ constant. Methane. Per cent.	CH ₄ -N ₂ constant. Oxygen. Per cent.	O ₂ -N ₂ constant. Hydrogen. Per cent.	H ₂ -N ₂ constant. Oxygen. Per cent.
Mixture for maximum speed of uniform movement of flame	9.9	24.8	38.5	23.4
Mixture in combining proportions. (Basic mixture)	9.5	19.0	29.6	14.8
Displacement	0.4	5.8	8.9	8.6

The addition of either combustible gas or oxygen to the basic mixture results in an increase in speed of the flame. According to the laws of mass action, it would be expected that the displacement would be greater on the addition of oxygen than on the addition of methane (since one molecule of methane combines with two molecules of oxygen for complete combustion); this is found to be so. The displacement should be less with oxygen than with hydrogen (since two molecules of hydrogen combine with one molecule of oxygen); experiment again shows this deduction to be correct. The fact that the specific heat of oxygen is lower than that of methane and much lower than that of hydrogen, however, would have the effect of decreasing proportionally the amount of displacement caused by excess of either of the two last-named gases. Thus the displacement caused by the addition of oxygen is found to be much greater than that caused by methane, but only a little less than that caused by hydrogen.*

*The Uniform Movement of Flame in Mixtures of Methane,
Oxygen, and Nitrogen.*

The speeds of the uniform movement of flame in mixtures of methane with atmospheres containing 13.7, 21, 33, 50, 66, and 100 per cent. of oxygen have been determined. The experiments were carried out in a horizontal glass tube, 2.5 cm. in diameter, as used for earlier experiments. A comparatively short tube, 1.5 metres in length, was used in order to avoid the development of the detonation-wave. With the fastest speeds of flames, however, the detonation-wave was developed after the flame had travelled less than a metre, so that for some of the experiments it was necessary to replace the last metre of the glass tube by a piece of lead piping of the same length and internal diameter.

Only the slowest speeds, up to about 300 cm. per second, were determined by means of the automatic commutator and single recording stylus usually employed for such work in this laboratory; for faster speeds recourse was had to delicate Deprez indicators with separate styli for each screen-wire recording on a smoked paper chart fixed to a rapidly revolving drum. The fastest speeds in mixtures of methane with pure oxygen were determined photographically by the method described by Mason and Wheeler (T., 1919, 115, 578). A comparison between the two last-named methods of recording speeds of flames gave closely agreeing results.

The results of the determinations are given in table III, and

* These experiments explain why the displacement of the maximum-speed mixture was found to be so small with the mixtures of producer gas and air, as described in Part III.

TABLE III.

Speed of Uniform Movement of Flame in Mixtures of Methane with Different Atmospheres of Nitrogen and Oxygen in a Horizontal Glass Tube 2.5 cm. in Diameter.

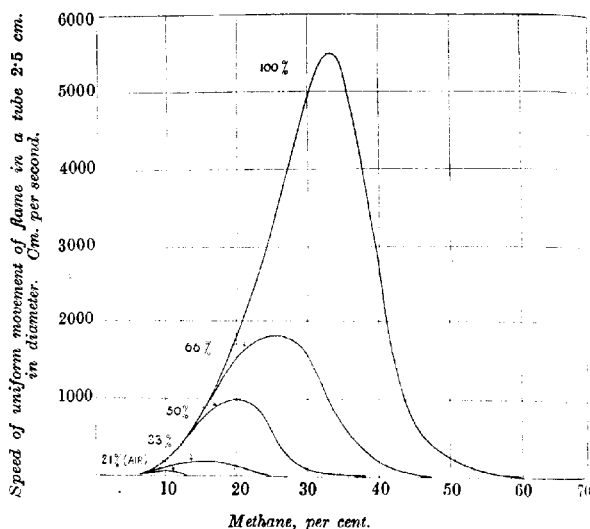
13.7 per cent. O ₂ .			Atmosphere, 33 per cent. O ₂ .			Atmosphere, 50 per cent. O ₂ .			Atmosphere, 66 per cent. O ₂ .			Atmosphere, 100 per cent. O ₂ .		
P'or cont.	Speed		P'or cont.	Speed		P'or cont.	Speed		P'or cont.	Speed		P'or cont.	Speed	
CH ₄ .	(cm. per sec.)		CH ₄ .	(cm. per sec.)		CH ₄ .	(cm. per sec.)		CH ₄ .	(cm. per sec.)		CH ₄ .	(cm. per sec.)	
6.41*	21.9		5.78	23.0		5.83	22.8		5.84	21.3		5.72	19.9	
6.70	21.0		5.87	23.9		9.60	150		8.79	96.5		10.52	266	
6.90	19.1		8.44	97.6		12.48	401		11.75	430		15.53	722	
			11.01	168		15.38	735		15.07	861		21.63	2300	
7.02	6 cm.		14.58*	232		19.84*	967		18.41	1307		26.95	3391	
			18.01	200		24.01	711		25.08*	1622		33.00*	5502	
			21.61	49.1		28.47	171		29.29	1690		36.14	3340	
			25.12	18.9		33.58	44		34.65	576		40.00	3059	
			25.41	15 cm.		37.63	18.9		38.62	174		48.23	4823	
						39.26	15 cm.		46.93	19.4		53.36	28.8	
									47.50	4 cm.		59.23	18.9	
									47.63	4 cm.		59.50	30 cm.	

diagrammatically in Fig. 1. For the values for mixtures with air, reference should be made to the table in Part II (T., 1919, 115, 1448). The mixture marked with an asterisk in each column is that which contains methane and oxygen in combining proportions.

Fig. 1 may be compared, so far as its general characteristics are concerned, with the similar diagram given by Mason and Wheeler (*loc. cit.*, p. 1048) for mixtures of methane with atmospheres containing less oxygen than air. It should, however, be noted that these authors determined the speeds in a tube 5 cm. in diameter.

The most striking results are those for mixtures of methane with

FIG. 1.



pure oxygen. It will be seen that the maximum speed of the uniform movement of flame is obtained, as was anticipated, with the mixture containing methane and oxygen in combining proportions ($\text{CH}_4 + 2\text{O}_2$). This result is in sharp distinction from what obtains when the detonation-wave is developed in mixtures of methane and oxygen, for the mixture in which the speed of the detonation-wave is greatest contains equal proportions of methane and oxygen. The difference is the more striking when it is remembered that the uniform movement gives place to the detonation-wave after quite a short distance of travel of the flame.

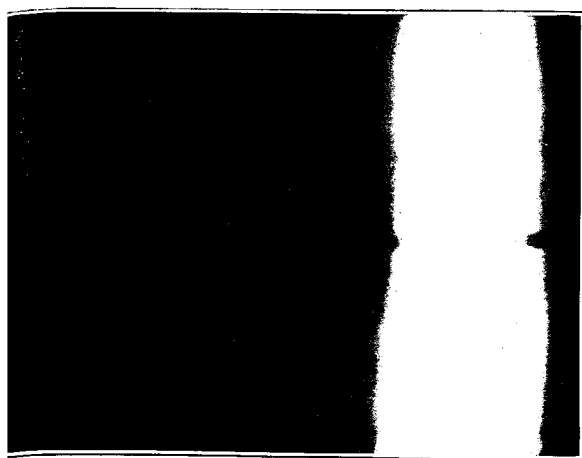


FIG. 3.

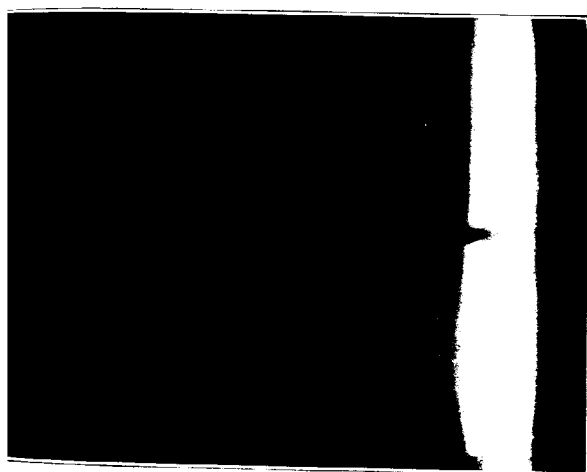
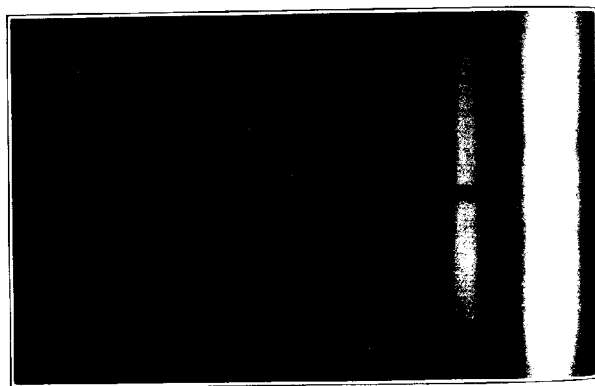
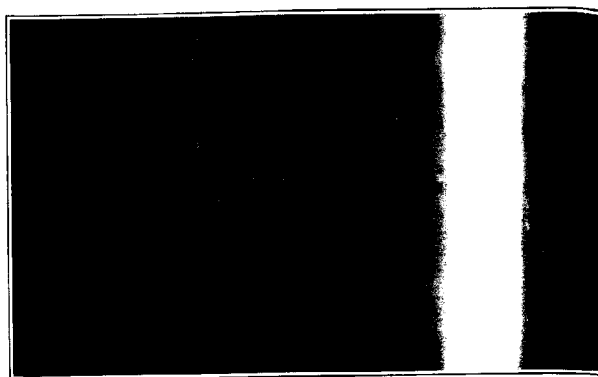


FIG. 2.



In table IV a comparison is made between the speed of the uniform movement and that of the detonation-wave in the five mixtures used by Dixon (*loc. cit.*, p. 181).

TABLE IV.

Comparison of the Speeds of the Detonation-wave and the Uniform Movement in Mixtures of Methane and Oxygen.

Composition of mixture.	Speed, metres per second.	
	Detonation wave. Tube 0.9 cm. diam.	Uniform movement. Tube 2.5 cm. diam.
$2\text{CH}_4 + 8\text{O}_2$	1963	18
$2\text{CH}_4 + 6\text{O}_2$	2146	33
$2\text{CH}_4 + 4\text{O}_2$	2322	55
$2\text{CH}_4 + 3\text{O}_2$	2470	25
$2\text{CH}_4 + 2\text{O}_2$	2528	2

The addition of methane to the mixture for complete combustion ($\text{CH}_4 + 2\text{O}_2$) is thus seen to increase the speed of the detonation-wave, but markedly to decrease the speed of the uniform movement of flame.

This effect is well illustrated by photographs of the flames (1) in mixture containing just sufficient oxygen for complete combustion of the methane, and (2) in a mixture containing rather more methane (40 per cent.). In the latter mixture (Fig. 2), the uniform movement persisted over about 25 cm. of travel of the flame, which then vibrated rapidly for a short time (0.06 sec.) without moving further along the tube. The vibrations were followed by a rapid acceleration of the flame, resulting in the detonation-wave, which shattered the glass tube at about 25 cm. distance from the lead extension piece. The bright band at the bottom of the photograph is caused by the "retonation-wave."*

Although the speed of the uniform movement of flame is slower in a mixture containing 40 per cent. of methane than in one containing 33 per cent., the detonation-wave is developed sooner in the former. With the 33 per cent. mixture, the uniform movement extends across the whole width of the photograph (Fig. 3). The incidence of the detonation-wave a short distance further along the tube (within the lead extension piece) is indicated by the right hand due to the retonation-wave, at the bottom of the photograph.†

* A compression-wave sent back, simultaneously with the development of the detonation-wave, through the burnt or still burning mixture (Dixon, *Phil. Trans.*, 1902, 200, 315).

† The length of tube photographed was 30 cm., and the speeds of the film were 592 and 752 cm. per second for Fig. 2 and Fig. 3 respectively.

It must be admitted that the displacement of the maximum-speed mixture away from that required for complete combustion is not very great in mixtures of methane and air. A better test of the soundness of the conclusion that with pure oxygen the maximum-speed mixture and the complete-combustion mixture should coincide should be obtained with a combustible gas like hydrogen. With this gas, it will be remembered, the maximum-speed mixture with air is displaced by as much as 10 per cent. Experiments were therefore made with mixtures of hydrogen and pure oxygen.

Three mixtures were examined, and the speeds are recorded in table V, with the speeds of the detonation-wave in the same mixture for comparison.

TABLE V.

Comparison of the Speeds of the Detonation-wave and the Uniform Movement in Mixtures of Hydrogen and Oxygen.

Hydrogen. Per cent.	Speed, metres per sec.	
	Detonation-wave. Tube 0.9 cm. diam. (Dixon).	Uniform movement. Tube 2.5 cm. diam.
59.9	2650	5.74
66.6	2824	6.62
75.2	3140	5.15

Fig. 4 and Fig. 5 are the photographs of the flames in the mixtures containing 75.2 per cent. and 66.6 per cent. of hydrogen respectively.* It will be seen that the photographs are similar in general character to those obtained with the two corresponding mixtures of methane and oxygen.

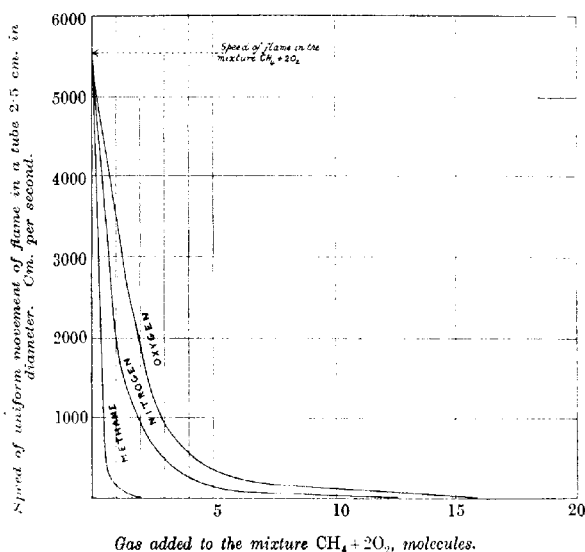
To revert to the experiments with methane, the addition of either methane or oxygen, like that of the inert gas, nitrogen, to the mixture of methane with pure oxygen of the composition $\text{CH}_4 + 2\text{O}_2$, results in a reduction of the speed of the uniform movement of flame. The relative effects of these three gases are shown in Fig. 6. Methane, having the highest specific heat of the three, has the greatest retarding effect. Although oxygen and nitrogen have approximately the same specific heat, the retarding effect of the former is appreciably less, owing to the effect of mass action when the gas added is capable of taking part in the reaction.

The application of the "speed generalisation" was shown in earlier papers to be restricted by the fact that the only data avail-

* The speeds of the films were 784 and 816 cm. per second for Fig. 4 and Fig. 5 respectively.

able for use in the calculations were those respecting mixtures of inflammable gases with air. Thus with methane-hydrogen-air mixtures no calculations could be made for mixtures in which the speed of flame was greater than 67 cm. per second, the maximum speed in mixtures of methane and air. The speeds now obtained in mixtures of methane with atmospheres containing more oxygen than air are often greater than the maximum speed with hydrogen-air mixtures, so that the use of these values should render it

FIG. 6.



possible to calculate the speeds of the uniform movement of flame in any methane-hydrogen-air mixture.

For this purpose, however, it would be necessary to determine the speed of flame in mixtures of hydrogen with different atmospheres in the same way as has been done for methane, and for similar calculations to be made for mixtures of an industrial gas with air, similar determinations would be required for each individual gas present in the industrial gas.

Such a series of determinations is outside the scope of the present work. It is, however, important to establish the fact that the "speed generalisation" is capable of extension in this manner.

To this end, a few determinations have been made for methane-hydrogen-air mixtures.

To simplify the calculations, mixtures of methane and hydrogen with just sufficient air for complete combustion were chosen. A curve similar to the one in Fig. 6 for $\text{CH}_4 + 2\text{O}_2 + x\text{N}_2$ was constructed for hydrogen ($2\text{H}_2 + \text{O}_2 + x\text{N}_2$). If mixtures are selected from these two curves in which the speed of flame is the same and is intermediate between the maximum speeds in methane-air and hydrogen-air mixtures, it is possible to mix them in such proportions that the resulting mixtures will contain nitrogen and oxygen in the ratio in which they are found in air. This mixture will have the same speed of uniform movement of flame, will contain combustible gas and oxygen in combining proportions, and will be, in a sense, a methane-hydrogen-air mixture. In this way, it is possible to determine the speed of flame in all mixtures of methane and hydrogen with sufficient air for their complete combustion. The results of such calculations with three simple mixtures are recorded in table VI.

TABLE VI.
Speed of Uniform Movement of Flame.

Hydrogen-Methane mixture.	Cm. per sec.		
	Found.	Calculated.	
		From curves.]	From formula.
$\text{H}_2 + 3\text{CH}_4$	85	90	95
$\text{H}_2 + \text{CH}_4$	135	140	149
$3\text{H}_2 + \text{CH}_4$	240	250	246

The results recorded in the last column are obtained by use of a formula similar to the one used in Part II (T., 1919, 115, 1452) for calculating the maximum-speeds of flame in mixtures with air, "mixture for complete combustion" being substituted for "maximum-speed" mixture.

The experimental work described in this series of papers was carried out at the Home Office Experimental Station under the general direction of Dr. R. V. Wheeler.

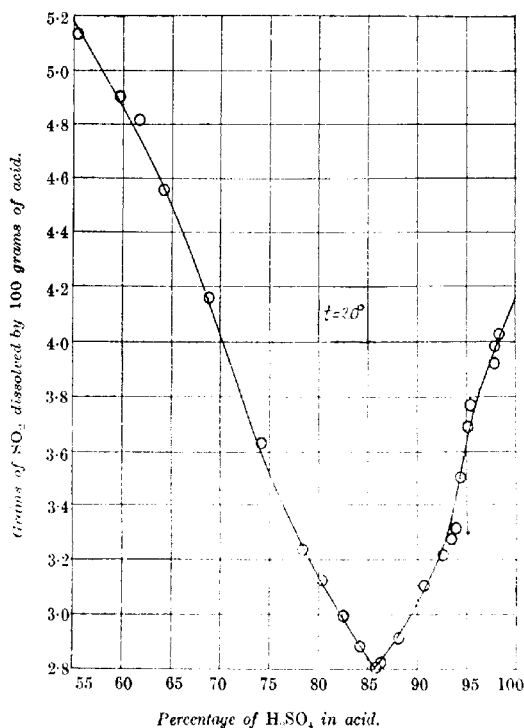
ESKEMEALS,
CUMBERLAND.

[Received, November 12th, 1919.]

VII.—*The Solubility of Sulphur Dioxide in Sulphuric Acid.*

By FRANK DOUGLAS MILES and JOSEPH FENTON.

IN the course of some work on the gas-purifying system of a plant for the manufacture of sulphuric acid by the "contact" process it was noticed that 95 per cent. sulphuric acid dissolved more sulphur



dioxide than did acid of 85 per cent. The solubility in more dilute acid diminishes in the usual manner as the concentration increases, so that the observation pointed to some peculiarity in the solubility curve for higher concentrations of acid. A determination of the

curve was therefore undertaken in the region most technically important, namely, with acid from 50 to 100 per cent., at 20°.

No sufficiently detailed measurements of this kind appear to have been made, although the coefficients of solubility have been given by Kolb for acid varying from 10 to 81 per cent. (*Bull. Soc. Ind. Mulhouse*, 1872, 222). The coefficients of solubility in acid of D 1·84, from 0° to 90°, have also been determined by Dunn (*Chem. News*, 1882, 45, 282).

To obtain rapid saturation of sulphuric acid, especially when the acid is concentrated, and therefore viscous, is by no means easy. It was found most satisfactory to use small amounts—15—20 grams—in thin test-tubes placed in a thermostat. The acid was stirred vigorously by means of a mechanical stirrer, while a stream of sulphur dioxide was passed in so that the mixture was churned into a froth exposing a very large surface to the gas. Precautions were taken to prevent admission of air to the tube, and to maintain the temperature at 20°±0·1.

Samples were obtained by rapidly drawing the saturated mixture, by means of slight suction, into small weighed glass bulbs, each holding about a gram and made by drawing out glass tubing, so that rather wide capillary ends remained. After sealing and weighing quickly, these bulbs were dropped, two for each analysis, into (1) *N*-sodium hydroxide in slight excess, (2) *N*/10-iodine in slight excess, mixed with 100 c.c. of water. The bulbs were broken and the titrations carried out as usual. Experiment showed that the concentrated sulphuric acid had no influence on the iodometric test.

Analyses were made in each experiment until the results were nearly constant. Generally, the acid-content tended to rise slightly on account of the drying action of the gas. The results are given below. The temperature was 20°, and a correction was applied when the barometer diverged appreciably from 760 mm.

Sulphuric acid. Per cent.	Sulphur dioxide dissolved by 100 grams of acid. Grams.	Sulphuric acid. Per cent.	Sulphur dioxide dissolved by 100 grams of acid. Grams.
55·1	5·13	88·1	2·9
59·6	4·90	90·8	3·10
61·6	4·82	92·8	3·21
68·9	4·16	93·7	3·27
74·1	3·63	94·0	3·31
78·3	3·23	94·6	3·50
80·2	3·12	95·5	3·69
82·5	2·99	95·6	3·77
84·2	2·88	96·5	3·83
85·3	2·83	98·0	3·98
85·8	2·80	98·5	4·03
86·5	2·82	—	—

These figures are shown graphically in the accompanying curve.

The solubility reaches a minimum value in sulphuric acid of 86.0 per cent., and from that point the curve inclines very sharply upward for either increase or decrease in percentage of sulphuric acid. It is significant that acid of 84.5 per cent. has the composition of the hydrate, $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, and that in the neighbourhood of this point the temperature of melting, and other physical properties, pass through critical values.

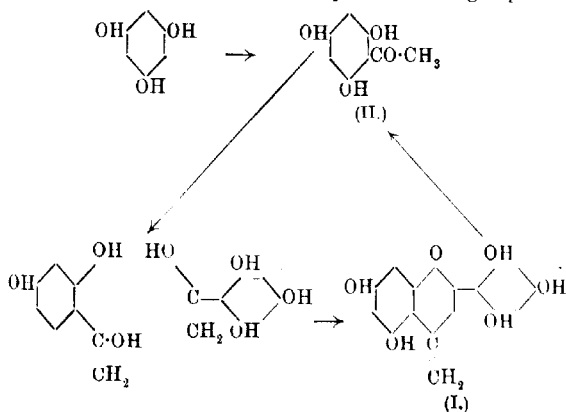
[Received, December 18th, 1919.]

VIII.—Phloroacetophenone.

By KIEMUD BEHARI SEN and PRAPHULLA CHANDRA GHOSH.

PHLOROACETOPHENONE is an important compound for the synthesis of many natural dyes (Goschke and Tambor, *Ber.*, 1912, **45**, 1237). Bülow and Wagner obtained it by first condensing phloroglucinol with benzoyl chloride and then degrading the resulting pyranol (*Ber.*, 1901, **34**, 1798). Leuchs and Sperling (*Ber.*, 1915, **48**, 135) prepared it by the action of water at 170° on Jordan's lactones (T., 1897, **71**, 1111). In no case was the direct synthesis achieved.

Resacetophenone, gallacetophenone, and similar compounds are easily and directly prepared from the corresponding phenols by heating them with acetic acid and zinc chloride. It was therefore thought that phloroglucinol on similar treatment might give phloroacetophenone, and thus a direct synthesis might be effected. When, however, phloroglucinol is heated with acetic acid and zinc chloride there is produced a yellow, crystalline compound dissolving in potass-



ium hydroxide solution with a pink colour and fluorescence. From the analysis and the determination of the molecular weight by the ebullioscopic method in alcohol it is concluded that phloroacetophenone is first formed, but that two molecules at once combine, giving a pyran derivative resembling Nencki's resacetin (p. 61).

On boiling the pyran derivative (I) with 10 per cent. sodium hydroxide solution the heterocyclic ring is broken and phloroacetophenone (II) is obtained.

The melting point of phloroacetophenone was found to be 284—285°; according to Bülow and Wagner, it does not melt up to 280°, and Leuchs and Sperling give 218°. The substance obtained by the latter authors contained one molecule of water of crystallisation, which may account for the difference in melting point.

EXPERIMENTAL.

5:7-Dihydroxy-2-o-o-p-trihydroxyphenyl-4-methylene-1:4-benzopyran (I).

Two grams of phloroglucinol were dissolved in 2 c.c. of glacial acetic acid, 3 grams of zinc chloride added, and the whole was gently boiled for ten to fifteen minutes. The yellow liquid was dissolved in hot hydrochloric acid and the clear solution, on cooling, deposited yellow needles (0.9 gram). The substance is soluble in alcohol, and dissolves in potassium hydroxide solution, giving a pink, fluorescent solution. It does not melt up to 290°:

0.1256 gave 0.2751 CO_2 and 0.0502 H_2O . $\text{C}=59.7$; $\text{H}=4.45$.*

0.5713, in 18 c.c. alcohol, gave $\text{E}=0.18^\circ$. $\text{M.W.}=275$.

$\text{C}_{16}\text{H}_{12}\text{O}_6, \text{H}_2\text{O}$ requires $\text{C}=60.3$; $\text{H}=4.4$ per cent. $\text{M.W.}=300$.

Acetyl Derivative.—One gram of the above compound, 10 c.c. of acetic anhydride, and a few drops of pyridine were boiled gently for an hour. The semi-solid mass obtained on pouring into water was dissolved in acetic acid and precipitated with water, being finally crystallised from dilute acetic acid. The compound melts at 80° and begins to decompose at about 90°:

0.1202 gave 0.2689 CO_2 and 0.0560 H_2O . $\text{C}=60.8$; $\text{H}=5.1$.

$\text{C}_{26}\text{H}_{22}\text{O}_{11}$ requires $\text{C}=61.16$; $\text{H}=4.31$ per cent.

Phloroacetophenone (II).

Three grams of the pyran were dissolved in 75 c.c. of 10 per cent. sodium hydroxide solution, the solution boiled for ten to twelve minutes, and, after cooling, acidified with dilute hydrochloric acid. The precipitate was collected, dried, and finally crystallised from a

mixture of alcohol and dilute hydrochloric acid. The product (0.8 gram) was almost colourless, and dissolved in potassium hydroxide solution with only a pale yellow colour. It melted at 284—285°. (Found, C=56.44; H=5.2. $C_8H_5O_4$ requires C=57.1; H=4.8 per cent.)

Phenylhydrazone.—This was prepared in the ordinary way by dissolving the phloracetophenone in a mixture of alcohol and acetic acid, adding a little more than the theoretical quantity of phenylhydrazine hydrochloride and sodium acetate, and warming for a few minutes. To the clear solution water was added, and the precipitate was collected, dried, and finally crystallised from dilute alcohol. It decomposes at 237—240°:

0.1150 gave 11.65 c.c. N_2 at 32° and 761 mm. $N=11.3$.

$C_{11}H_{14}O_3N_2$ requires $N=10.8$ per cent.

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IX.—The Peroxides of Bismuth.

By RICHARD ROBERT LE GEYT WORSLEY and PHILIP WILFRED ROBERTSON.

THE most comprehensive and recent work on the peroxides of bismuth is by Gutbier and Bünz (*Zeitsch. anorg. Chem.*, 1906, **48**, 163, 295; **49**, 433; **50**, 211). These observers, from their experiments on the oxidation of bismuth hydroxide in the presence of alkali hydroxide, drew the conclusion that chemical compounds could not be isolated from the mixtures thus obtained, even after subsequent treatment with nitric acid. It seemed, however, probable that continuous grinding with dilute nitric or glacial acetic acid might bring about a separation of the lower oxide of bismuth from the peroxide. Accordingly, preliminary experiments were carried out in which (a) bismuth hydroxide precipitated in the oxidising medium, and (b) ordinary bismuth trioxide, were treated with ammonium persulphate in boiling dilute sodium hydroxide solution. The first product was comparatively rich in bismuth peroxide, but its composition altered only little after grinding with glacial acetic acid; the product in the second case contained less peroxide, but, after several grindings, its composition approximated to that of bismuth tetroxide. Experiments were therefore made

in this manner with different oxidising agents in the presence of sodium or potassium hydroxide of different concentrations. In dilute solutions, bismuth tetroxide was the only product; in more concentrated solutions, higher oxides were also formed. These products were analysed in the following manner: the peroxidic oxygen was estimated (a) by distillation with hydrochloric acid (Bunsen's method), (b) when the substance was soluble, by dissolving in hot nitric acid (D 1.2) and measuring the liberated oxygen; the peroxidic oxygen plus water was determined by heating to redness. The compounds for which analytical results are given below were free from sodium or potassium.

Action of Chlorine on Bismuth Trioxide suspended in Boiling Alkali Hydroxide.

The duration of each experiment was about half an hour. The product of the reaction in dilute solution (5—10 per cent.) was either Bi_2O_4 (brown) or $\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (brown). The exact conditions determining the formation of the anhydrous oxide or the hydrate could not be ascertained. In concentrated alkali hydroxide (35—40 per cent.) there was formed a mixture of $\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (red) and $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (yellow), from which the lower oxide could be fractionally separated by the action of hot nitric acid (D 1.4). The following values were obtained in one typical experiment for a mixture: (A) after two grindings with glacial acetic acid; (B) after three grindings with glacial acetic acid; (C) after one extraction with hot nitric acid; (D) after two extractions with hot nitric acid:

	A.	B.	C.	D.
Peroxidic-O	5.20	5.05	3.94	3.47
Peroxidic-O + H_2O	10.05	10.02	9.97	10.00

$\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ requires O = 3.10; O + H_2O = 10.08 per cent.

$\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$ requires O = 6.22; O + H_2O = 9.73 per cent.

According to Deichler (*Zeitsch. anorg. Chem.*, 1899, **20**, 111), the product of the reaction should be a mixture of Bi_2O_4 and $\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$, and the $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ is produced by the action of nitric acid on the latter. The colour of the substance A (orange-red), the analytical results, and its behaviour with nitric acid all indicate that it was a mixture of $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (yellow) and $\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (red).

Action of Ammonium Persulphate or Potassium Ferricyanide on Bismuth Trioxide suspended in Boiling Alkali Hydroxide.

The product of the reaction in dilute solution was either Bi_2O_4 (brown or purplish-black) or $\text{Bi}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (brown or purplish-black).

The experimental conditions determining the formation of these four varieties could not be ascertained. In concentrated alkali there was formed, in addition to Bi_2O_4 or $\text{Bi}_2\text{O}_4\cdot\text{H}_2\text{O}$, a small amount of Bi_2O_6 (yellow), which could be fractionally separated from the lower oxide by the action of hot nitric acid (D 1.2).

Bismuth Tetraoxide, $\text{Bi}_2\text{O}_4(\text{BiO}_2)$.

This was prepared by the action of chlorine, ammonium persulphate, or potassium ferricyanide on bismuth trioxide suspended in a dilute solution of boiling alkali hydroxide, and the following modifications have been obtained: I, Bi_2O_4 (brown); II, Bi_2O_4 (purplish-black); III, $\text{Bi}_2\text{O}_4\cdot\text{H}_2\text{O}$ (brown); IV, $\text{Bi}_2\text{O}_4\cdot\text{H}_2\text{O}$ (purplish-black).

The following are typical analyses for preparations which had been ground with glacial acetic acid in an agate mortar until they were completely free from bismuth trioxide and occluded alkali hydroxide:

	I.	II.	Bi_2O_4
Peroxidic-O	3.31	3.26; 3.20*	3.33 per cent.
Loss on heating	3.27	3.24 3.61	3.33 „
	III.	IV.	$\text{Bi}_2\text{O}_4\cdot\text{H}_2\text{O}$.
Peroxidic-O	3.25; 3.07	3.13; 3.21	3.21 per cent.
Peroxidic-O + H_2O	6.88; 6.20	6.22; 6.92	6.83 „

* Determined gasometrically.

The brown and purplish-black anhydrous bismuth tetraoxides appear to be physical isomerides, and are both stable at 100° . The modifications with one molecule of water lose the water in a vacuum (1 mm.) over phosphoric oxide, slightly darkening in colour. At 100° in the steam-oven, they lose half this amount:

	III.	IV.
Loss at 100°	1.70, 1.74	1.89
$\text{Bi}_2\text{O}_4\cdot\text{H}_2\text{O}$ requires $\frac{1}{2}\text{H}_2\text{O}$ = 1.81 per cent.		

At 160° all varieties decompose, with the liberation of oxygen.

Bismuth tetraoxide is soluble in nitric acid (D 1.2) at 70 – 90° , yielding its peroxidic oxygen in the gaseous form (with small quantities of ozone). It is peculiarly reactive, immediately oxidising manganous salts in the presence of dilute nitric acid, even in the cold. Bismuth tetraoxide is very sparingly soluble in concentrated alkali hydroxide, with the formation of an unstable persalt.

Another distinct variety, $\text{Bi}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (yellow), is formed, together with $\text{Bi}_2\text{O}_3\cdot\text{H}_2\text{O}$, by the action of chlorine on bismuth

trioxide in boiling concentrated alkali hydroxide. It may be fractionally separated from the higher oxide by treatment with boiling nitric acid (D 1.4), in which it is only sparingly soluble. The following analyses were obtained for two preparations:

	I.	II.	$\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$.
Peroxidic-O	3.47	3.38	3.10 per cent.
Peroxidic-O + H_2O	10.00	9.95	10.08 ..

At 100° it decomposes, darkening in colour, with the loss of both oxygen and water.

Bismuth Pentoxide, Bi_2O_5 .

The monohydrate, $\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (red or brown), soluble with difficulty in hot concentrated nitric acid, is obtained (a) mixed with $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ by the action of chlorine on bismuth trioxide in boiling concentrated alkali hydroxide, (b) in small quantities mixed with $\text{Bi}_2\text{O}_4 \cdot \text{H}_2\text{O}$ by the action of ammonium persulphate on bismuth trioxide in dilute alkali hydroxide at 40 – 60° , when the action is allowed to continue for five to six hours. The bismuth pentoxide produced by the first method could not be separated from the admixed $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; obtained according to the second reaction, it could be completely separated from the $\text{Bi}_2\text{O}_4 \cdot \text{H}_2\text{O}$ by extraction with hot nitric acid (D 1.2). Three different samples gave the following values on analysis:

	I.	II.	III.	$\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$.
Peroxidic-O	5.97	6.05	6.26	6.22 per cent.
Peroxidic-O + H_2O ...	9.80	—	10.16	9.73 ..

A second variety, $\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (brown), readily soluble in hot nitric acid (D 1.2), is obtained from commercial sodium bismuthate after repeated grinding with glacial acetic acid. The following analyses were obtained for three different preparations:

	I.	II.	III.	$\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$.
Peroxidic-O	6.20*	6.19*	6.14	6.22 per cent.
Peroxidic-O + H_2O ...	10.00	9.91	9.96	9.73 ..

* Determined gasometrically.

Anhydrous bismuth pentoxide would appear to be incapable of existence. The hydrate, when left in a vacuum (1 mm.) over phosphoric oxide, darkens in colour and slowly loses water and oxygen. At 100° the decomposition is more rapid; in one experiment the percentage of peroxidic oxygen fell from 6.2 to 1.9 in twenty days, and subsequently remained constant, indicating that bismuth trioxide and bismuth tetroxide had been formed in approximately equal amounts.

Bismuth Hexoxide, $\text{Bi}_2\text{O}_6(\text{BiO}_3)$.

Bismuth hexoxide is obtained in small quantities by the action of ammonium persulphate or potassium ferricyanide on bismuth trioxide suspended in boiling concentrated alkali hydroxide, together with bismuth tetroxide (Bi_2O_4 or $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$), from which it can be separated by continuous extraction with warm nitric acid (D 1.2). It may also be prepared by the oxidation of the tetroxide and subsequent treatment of the product with nitric acid. Bismuth hexoxide is pale brown and contains no water. At the ordinary temperature it loses oxygen slowly, darkening in colour. This would explain the slightly low results obtained on analysis:

	I.	II.	Bi_2O_6 .
Peroxide-O.....	8.96	9.13	9.37 per cent.
Loss on heating	9.00	9.11	9.37 „

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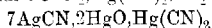
X.—The Action of Mercuric Cyanide on Metallic Salts.

By LILANANDA GUPTA.

The action of mercuric cyanide on different metallic salts has been the subject of investigation by previous workers, for example, Poggiale (*Compt. rend.*, 1846, **23**, 762). Varet (*Bull. Soc. chim.*, 1891, [iii], **5**, 8). Bloxam (*Ber.*, 1883, **16**, 2669), etc. In this paper, the action of mercuric cyanide on the chlorides of copper, cobalt, nickel, manganese, cadmium, chromium, vanadium, and aluminium, the nitrates of silver and lead, and ammonium molybdate has been studied. The method of procedure was, however, somewhat different from that adopted by Poggiale and others. A concentrated solution of mercuric cyanide was added to an excess of the salt solutions, and the mixture evaporated slowly on the water-bath. The precipitate which was obtained in each case was collected and washed, as a rule, with the minimum quantity of cold water, and next with alcohol. In the case of the aluminium compound, the concentrated solution was evaporated in a vacuum, and the crystals obtained were washed with alcohol alone.

It is to be noted that the general method of preparing a double cyanide of two metals is to bring together their respective cyanides

or to treat an alkali cyanide with some other double cyanide of the metals in question. The action of mercuric cyanide on the chlorides of copper and cobalt and silver nitrate producing, respectively, the compounds $\text{CuCN} \cdot 2\text{Hg}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{CN})_3 \cdot \text{Hg}(\text{CN})_2 \cdot 5\text{H}_2\text{O}$, and $\text{AgCN} \cdot \text{Hg}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$, described in this paper, are thus exceptions to this general rule. On the other hand, Poggiale and Bloxam mention the compounds $2\text{CoCl}_2 \cdot \text{Hg}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$ and



as the products of reaction. Hofmann and Wagner (*Ber.*, 1908 41, 319), however, obtained the salt $\text{AgNO}_3 \cdot \text{Hg}(\text{CN})_2 \cdot 2\text{H}_2\text{O}$ in the last case.

Other compounds described in this paper are $4\text{AlCl}_3 \cdot \text{HgCl}_2 \cdot 28\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot \text{Hg}(\text{CN})_2 \cdot 2\text{H}_2\text{O}$. Cryoscopic determinations of the molecular weights in aqueous solutions of these salts have been carried out; also measurements of the conductivity of the latter salt were made at different dilutions.

EXPERIMENTAL.

Compound $\text{CuCN} \cdot 2\text{Hg}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$.

About 24 grams of cupric chloride were dissolved in 100 c.c. of water, and a solution of mercuric cyanide containing 10 grams of the salt was added, the final volume of the mixture being 300 c.c. This was evaporated slowly on the water-bath almost to one-third its original bulk, and was set aside. Next morning, a very fine precipitate had formed, which was collected, washed first with cold water, and finally with alcohol, and dried on a porous plate at 25°.

The product had a pale violet colour, shining like fine sand when held in the sunlight, and under the microscope was seen to consist of cubes. It is not appreciably soluble in water, but decomposes and passes into solution when treated with sulphuric acid:

- I. 0.2011 gave 0.0258 CuO . $\text{Cu} = 10.25$.
 0.2786 „ 0.1680 Hg . $\text{Hg} = 60.32$.
 0.2161 „ 18.6 c.c. N_2 at 24° and 760 mm. $\text{CN} = 18.21$.
 II. 0.2125 „ 0.0262 CuO . $\text{Cu} = 9.97$.
 III. 0.2618 „ 0.0318 CuO . $\text{Cu} = 9.70$.
 0.3242 „ 0.1960 Hg . $\text{Hg} = 60.46$.
 0.2838 „ 26.2 c.c. N_2 at 32° and 760 mm. $\text{CN} = 18.39$.
 $\text{CuCN} \cdot 2\text{Hg}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$ requires $\text{Cu} = 9.47$; $\text{Hg} = 60.15$; $\text{CN} = 19.54$
 per cent.

Compound $\text{Co}(\text{CN})_3 \cdot \text{Hg}(\text{CN})_2 \cdot 5\text{H}_2\text{O}$.

This was prepared by the action of mercuric cyanide on cobalt chloride. The proportions of the salts were as 1:3, and the method

of procedure was exactly the same as mentioned above. A visible reaction took place within ten minutes from the start; the colour of the solution deepened, and slow precipitation commenced. The washings and drying were performed as before.

The compound is sparingly soluble in water, but decomposes and passes into solution by the action of sulphuric acid, as is the case with all sparingly soluble cyanides:

0.3118 gave 0.043 Co. Co=12.79.

0.2440 „ 0.0977 Hg. Hg=40.04.

0.1875 „ 25.46 c.c. N_2 at 26° and 760 mm. CN=27.78.

$Co(CN)_3.Hg(CN)_2.5H_2O$ requires Co=12.31; Hg=41.40; CN=27.13 per cent.

Nickel Cyanide, $Ni(CN)_2.3H_2O$.

About 20 grams of nickel chloride, $NiCl_2.6H_2O$, were dissolved in 100 c.c. of water, and to the cold solution was added a filtered solution of mercuric cyanide (8:100). The details of the procedure were exactly the same as in the foregoing cases.

Williams ("Cyanogen Compounds," p. 65) describes the compound, $Ni(CN)_2.7H_2O$, which he obtained by treating an alkali cyanide with excess of a nickel salt. The compound obtained by the above method is not at all gelatinous, it has a fine, granular structure, and is insoluble in water or dilute acids, but is decomposed by concentrated sulphuric acid. Two preparations gave the same product in each case:

I. 0.3852 gave 0.1751 NiO. Ni=35.71.

0.2348 „ 35.4 c.c. N_2 at 0° and 760 mm. CN=31.61.

II. 0.2605 gave 0.1186 NiO. Ni=35.78.

0.4348 „ 0.1408 H_2O . H_2O =32.38.*

$Ni(CN)_2.3H_2O$ requires Ni=35.75; CN=31.51; H_2O =32.74 per cent.

The estimation of water in this compound and in subsequent determinations was carried out in the following manner.

In a combustion furnace was placed a hard-glass combustion tube containing a known amount of the substance to be dehydrated in a weighed porcelain boat. One end of this tube was joined successively to a sulphuric acid wash-bottle, a calcium chloride U-tube, a soda-lime tower, a second sulphuric acid wash-bottle, and finally to an air-supply. To the other end, a U-tube containing pumice stone soaked in sulphuric acid was attached. A guard tube containing calcium chloride was also joined to this U-tube. A thermometer was inserted through an opening at the top of the

* The dehydration was completed at 170° .

furnace just above the glass tube. Air-tight joints were secured, and blank experiments were previously conducted. The boat containing the salt was placed at the end furthest from the U-tube containing pumice stone. The heating was gradual, and began from the opposite end. A regular stream of dry air was passed through the combustion tube, and the water set free from the substance was condensed and collected in the weighed U-tube containing pumice stone soaked in sulphuric acid. It was finally weighed again, and the difference between the two weights gave the amount of water in the compound.

Compound $\text{AgCN}, \text{Hg}(\text{CN})_2, 4\text{H}_2\text{O}$.

To 100 c.c. of a solution of silver nitrate containing 12 grams of the salt was added a filtered solution of 6 grams of mercuric cyanide in 100 c.c. of water. This mixture was allowed to evaporate to half its original bulk. A slight turbidity was noticed almost from the beginning. From the ice-cold concentrated solution, milk-white needles were deposited within ten minutes. These were collected and washed, first with a little water, then with alcohol, and dried on a porous plate at 25° .

The compound decomposes slightly in the presence of water and dissolves in dilute sulphuric acid:

I. 0.8172 gave 0.2403 AgCl and 0.4166 HgS. Ag = 22.12; Hg = 43.94.

0.2735 gave 22.2 c.c. N_2 at 30° and 760 mm. CN = 17.64.

II. 0.5797 gave 0.1751 AgCl and 0.2998 HgS. Ag = 22.73; Hg = 44.59.

0.7988 gave 0.1196 H_2O * H_2O = 14.97.

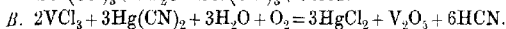
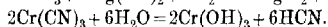
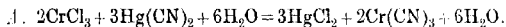
$\text{AgCN}, \text{Hg}(\text{CN})_2, 4\text{H}_2\text{O}$ requires Ag = 23.5; Hg = 43.66; CN = 17.07; H_2O = 15.77 per cent.

Action of Mercuric Cyanide on Chromium Trichloride and Vanadium Trichloride.

The action of mercuric cyanide on the above-mentioned salt solutions was tried in a similar manner, but the attempt to bring about a combination failed, and the product obtained in each case consisted of an oxide of the respective metal. The cyanides were no doubt formed at first, but these, being unstable, decomposed into

* The salt began to give off water from 85° onwards and the dehydration was completed at 180° .

the oxide and free hydrocyanic acid, the odour of the latter being distinctly perceptible. Thus:



Action of Mercuric Cyanide on Ammonium Molybdate and Lead Nitrate.

These reactions also failed to yield the expected cyanides; with ammonium molybdate was obtained metallic mercury in the shape of fine globules, and the oxide, Mo_2O_3 , as a violet-black powder, whilst in the latter case lead oxide was produced.

Compound $\text{MnCl}_2\cdot\text{Hg}(\text{CN})_2\cdot 2\text{H}_2\text{O}$.

About 25 grams of manganese chloride were dissolved in 150 c.c. of water, and a solution of mercuric cyanide (10:100) was added. The mixture was evaporated on the water-bath for one and a-half hours, and the bulk reduced to 100 c.c. This concentrated solution was well stirred and allowed to cool overnight. Next morning, a crystalline mass of pinkish-white scales had formed, which was powdered, washed with the mother liquor, and finally with alcohol. The compound was dried on a porous plate for two days at $24-25^\circ$. This salt was found to be dihydrated, whereas Poggiale described it as being trihydrated. It is very readily soluble in water, and under the microscope appears to consist of prismatic crystals:

I. 0.1617 gave 0.056 $\text{Mn}_2\text{P}_2\text{O}_7$ and 0.0918 HgS . $\text{Mn}=13.41$;
 $\text{Hg}=48.97$.

0.1617 gave 0.1197 AgCl . $\text{Cl}=18.32$.

0.3274 „ 18.8 c.c. N_2 at 24° and 760 mm. $\text{CN}=12.14$.

II. 0.2084 gave 0.0724 $\text{Mn}_2\text{P}_2\text{O}_7$ and 0.1180 HgS . $\text{Mn}=13.44$;
 $\text{Hg}=48.81$.

0.2084 gave 0.1485 AgCl . $\text{Cl}=17.63$.

0.8353 „ 0.0780 H_2O . $\text{H}_2\text{O}=9.34$.*

$\text{MnCl}_2\cdot\text{Hg}(\text{CN})_2\cdot 2\text{H}_2\text{O}$ requires $\text{Mn}=13.28$; $\text{Hg}=48.30$; $\text{Cl}=17.15$;
 $\text{CN}=12.56$; $\text{H}_2\text{O}=8.71$ per cent.

The conductivity of the salt at different dilutions was determined.

* The salt began to give off water from 80° onwards. The dehydration was completed at 170° .

$T = 23^{\circ}$.

Dilution.	Molecular conductivity.	μ_{∞} for zinc chloride.
V.	μ_{∞}	
50	204	207
100	212	216
500	237	231
1000	245	235

The molecular conductivity of zinc chloride at 23° for different dilutions is quoted from Kohlrausch's table, and proves to be almost identical with that of the salt. Assuming the molecular conductivity of zinc chloride and manganese chloride to be the same, as has been shown to be true by Kohlrausch, then the above compound evidently undergoes dissociation in solution into the ions Mn^{++} and Cl^{-} and the undissociated molecule $Hg(CN)_2$. This is confirmed by the fact that when treated with silver nitrate, silver chloride, but no silver cyanide, is formed. The determination of the molecular weight of the compound by the cryoscopic method supports the above view.

Solvent, 19.86 grams of water.

	Solute.	Δt .	M.W.
1	0.4593	-0.40°	107.3
2	0.9031	-0.75	112.0

M.W. calculated for no dissociation = 414.

M.W. calculated for dissociation to Mn^{++} , Cl_2^{-} and $Hg(CN)_2$ = 103.5.

Compound $4AlCl_3.HgCl_2.28H_2O$.

About 25 grams of hydrated aluminium chloride were dissolved in 100 c.c. of water, and a cold solution of 10 grams of mercuric cyanide in 100 c.c. of water was added. The mixture was evaporated to about 50 c.c., and as no deposit was obtained on allowing the solution to remain overnight, it was placed in a vacuum desiccator over sulphuric acid. After a day, a crystalline crust was found to have been formed on the surface of the solution. This was broken, and the crystallisation in a vacuum allowed to proceed for a further couple of days. During this interval, the crust on the surface was broken from time to time, and throughout the whole process of evaporation a strong odour of hydrocyanic acid was noticed. The crystals were collected, washed first with the mother liquor and then repeatedly with alcohol. The compound was finally dried in a vacuum for two days:

- I. 0.4973 gave 0.0877 HgS and 0.0804 Al_2O_3 . Hg=15.19;
Al=9.51.
0.4348 gave 0.6548 AgCl. Cl=36.43.
- II. 0.4407 gave 0.0777 HgS and 0.0790 Al_2O_3 . Hg=15.20;
Al=8.57.
0.5995 gave 0.8831 AgCl. Cl=37.25.
- $4\text{AlCl}_3, \text{HgCl}_2, 28\text{H}_2\text{O}$ requires Hg=15.27; Al=8.25; Cl=37.96;
 H_2O =38.52 per cent.

Cryoscopic Determination of the Molecular Weight.

Solvent, 15.7251 grams of water.

	Solute.	$\Delta t.$	M.W.
1	0.0963	-0.087°	130.84
2	0.3077	-0.277	130.94
3	0.6055	-0.515	137.10

The value found in this way approximates to one-tenth of the molecular weight, namely, 1309. In aqueous solution, the double salt is decomposed, as the solution is found to be distinctly acid. Since the compound $4\text{AlCl}_3, \text{HgCl}_2, 28\text{H}_2\text{O}$ is completely hydrolysed to hydrochloric acid, aluminium hydroxide, and mercuric chloride, the observed molecular weight ought to be one-twelfth of 1309, as the lowering of the freezing point, due to the aluminium hydroxide and mercuric chloride, is quite negligible. This anomaly is difficult to explain, and the molecular weight determination does not, therefore, furnish much evidence as to the true molecular weight of the double salt in solution.

I avail myself of this opportunity to express my sincere thanks to Sir Prafulla Chandra Ray for his helpful interest and encouragement in this work.

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